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THEIR CHEMISTRY AND METALLURGY

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EDITORIAL

During recent years the technical importance of what are usually called the less-common metals has been growing rapidly. The increasing need for publication in this field is, however, only partly catered for by the existing national chemical and metallurgical periodicals, and the great scattering of publications through the literature constitutes a serious handicap for those who wish to keep abreast with the new developments in the study of these metals.

The Journal of the Less-Common Metals is intended to meet the need for an international medium for publication of work on the advancement of the chemistry and metallurgy of all metals which can justifiably be considered as falling within the orbit of its title. It is not intended to restrict the Journal to a specific group of metals. The field is obviously a wide one and it would in fact be impossible to circumscribe it exactly. Papers will not be limited rigidly to less-common metals. For example, work on the platinum group will be included and new work on alloy systems in which only one of the metals can be described as less-common will be considered. Occasionally, papers that do not actually deal with these metals but have a bearing on their field of application will be published. A few of the twenty Symposium papers which constitute the greater part of the first two issues fall within this category; it is felt that they add considerably to knowledge on the important subject covered by the Symposium.

THE STUDY OF METALS AND ALLOYS ABOVE 1200°C

The papers which constitute the whole of the first issue of the Journal and the greater part of the second were read at a Symposium on the Study of Metals and Alloys above 1200°C which was held at Oxford (Great Britain) on the 17th and 18th September 1958. The Symposium was arranged by the Department of Metallurgy, The University Museum, Oxford, where an exhibition of apparatus and materials of interest in connection with refractory metals was held. The meetings took place in the Lecture Theatre of the Inorganic Chemistry Laboratory by kind permission of Dr. F. M. Brewer, and were attended by 107 metallurgists, from 34 laboratories, including visitors from Germany, Austria, Canada and Belgium.

In his introductory address, Professor W. Hume-Rothery welcomed the delegates, and emphasized the importance of the subject under discussion. He said that the newspapers were full of sensational articles on possible developments of nuclear energy, and of spectacular projects for flights to the moon. In practice the realisation of these possibilities depends to a great extent on the solution of metallurgical problems, many of which directly involve the properties of metals and alloys at high temperatures. The practical use of alloys at very high temperatures depends firstly on the development of alloys that retain their strength at the temperatures concerned, and secondly on the protection of these alloys from oxidation. It had been agreed that the Symposium should not deal with the problem of resistance to atmospheric attack at high temperatures.

Four Sessions were held dealing with high melting alloys, experimental methods, physical properties and mechanical properties.

The splitting up of a series of papers covering a specific topic was considered to be undesirable, and these Symposium papers are therefore published in this Journal in the order in which they were presented.

METALS AND ALLOYS OF THE PLATINUM GROUP

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REACTIONS OF PLATINUM METALS WITH REFRACTORY MATERIALS

Under certain conditions the six platinum metals possess a high reactivity at elevated temperatures, which is of importance in melting and annealing processes. In a reducing atmosphere, even at relatively low temperatures, they react rapidly with all refractory materials. Thus, during annealing of platinum in silica-containing tubes in the presence of hydrogen, even at a temperature below 1200°C, reduction of silica and contamination of the platinum with silicon with the formation of a low-melting eutectic occur. In a neutral, or even better a slightly oxidizing atmosphere, platinum may be melted in silica without any appreciable reaction. Similarly all other refractory materials, such as alumina or lime, may cause severe contamination during melting or high-temperature annealing under reducing conditions. Contamination of the metals of the platinum group by refractory materials at high temperatures may also occur under vacuum or in a neutral atmosphere, but generally the velocity of the reaction is slow, so that the contamination is much less than in a reducing atmosphere.

REACTIONS OF PLATINUM METALS WITH OXYGEN

We may mention the known reactivity of platinum with phosphorus, and that of palladium with sulphur[1,2,3]. Of special interest are the reactions between oxygen and the platinum metals at high temperatures. Ruthenium and osmium form volatile tetroxides. The other platinum metals volatilize with oxygen at temperatures at which the normal oxides have a dissociation pressure of oxygen much greater than one atmosphere. According to LACROIX[4] the ratio in which platinum volatilizes with oxygen in air is 2:1, and in oxygen 1:2, but generally the existence of an oxide with a definite composition is improbable.

Palladium takes up appreciable quantities of oxygen into solid solution[5]. Fig. 1 shows the weight-changes of palladium in oxygen at temperatures between 900 and 1300°C. At the lower temperatures there is a slow absorption of oxygen and the weight increases. Between 1100 and 1300°C there is rapid absorption of oxygen, but the increase in weight reaches a maximum after a certain time. After longer times the weight falls again owing to volatilization. At a temperature of about 1200°C palladium dissolves nearly 0.4 at.-% O, which is given off again during slow cooling. At 1300°C the differences in the volatilization of platinum, rhodium and palladium are small. At lower temperatures platinum volatilizes more quickly than rhodium and palladium. Of the four face-centred cubic platinum metals at high temperatures,

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iridium shows the greatest volatilization in the presence of oxygen, although in a vacuum it volatilizes least rapidly.

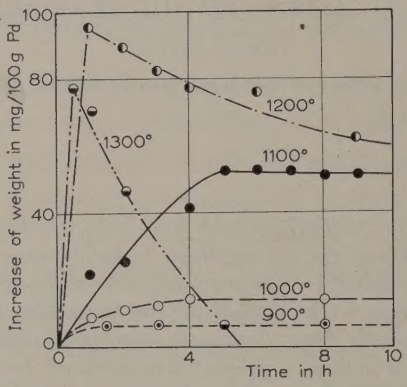

Fig. 1. Weight increase of palladium during annealing in oxygen.

After annealing in oxygen at high temperatures, the platinum metals show the characteristics of thermal etching, as illustrated in Fig. 2. The temperature at which the thermal etching of platinum metals occurs is so high that a surface-diffusion of the atoms in the direction of the lowest free surface energy takes place. The structure of the surface therefore is not only formed by volatilization, but also by the formation of the new surface profile by diffusion under the influence of an adsorbed oxygen

Fig. 2. Thermal etching of platinum in oxygen at 1300°C (× 1500).

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layer. If volatilization alone forms the surface, the sharp profile, given in Fig. 2, no longer appears, and normal etching occurs. Fig. 3 represents iridium alloys with 10 and 30% Ir after annealing in oxygen at 1100°C. The alloy with 10% Ir still has a sharp surface profile. At 30% Ir the volatilization of iridium is marked and normal deep etching is observed. In platinum–iridium alloys, therefore, an oxidizing atmos-

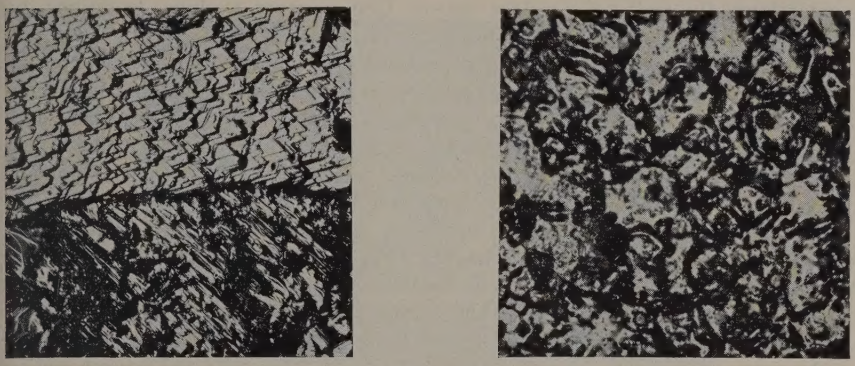

Fig. 3. Thermal etching of platinum–iridium alloys in oxygen at 1100°C, 23 h. Left: 10% Ir; right: 30% Ir.

phere at high temperatures may cause trouble by changing the composition of the alloys owing to preferred volatilization of one of the components. At lower annealing temperatures, at which the normal oxides are still stable, scaling may occur after the formation of the most stable oxides. Therefore, in alloys of platinum metals with one another, that with the highest energy of formation of the oxide will be preferentially oxidized.

In all alloys of platinum metals with metals of high oxygen affinity, these metals oxidize in presence of oxygen. The oxidation is arrested by the solubility of oxygen in the metals at high temperature, so that internal oxidation occurs, which often causes difficulties in experimental investigations. For certain alloys it is also necessary to avoid not only reducing substances or oxygen but also nitrogen.

For the melting of platinum metals, and their alloys with one another, a slightly oxidizing atmosphere may yet be allowed if ruthenium and osmium are absent. In all other cases it is necessary to work in a high vacuum or an inert atmosphere such as pure argon; the vacuum required is about 10^{-5} mm Hg.

MANUFACTURE OF ALLOYS

For manufacturing the alloys, it is often useful to combine the methods of sintering techniques with those of melting. It is very difficult to manufacture high-melting alloys by sintering alone, when no intermetallic compounds with high heats of formation exist, because it is almost impossible to bring these alloys to the thermodynamical equilibrium by diffusion in the solid state. For this reason melting is always to be preferred.

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The induction furnace offers many advantages. It is easy to control the atmosphere and to reach the desired vacuum, but contamination by refractory materials often cannot be avoided. In the vacuum arc furnace no contamination of the melt by the water-cooled copper crucible occurs. For scientific work the quantities to be melted are often small, and may not exceed about 2 g. It is thus not possible to melt the specimens as consumable electrodes, but a tungsten electrode usually does not contaminate the melt to a serious extent. Under proper working conditions, no tungsten can be spectroscopically detected in the melted alloys.

With the tungsten arc furnace it is not possible to work in a high vacuum. Melting must be done in purest argon with a pressure of about 30 to 100 mm Hg. With tungsten arc melting, therefore, proper removal of gases is not attained, especially with alloys of platinum metals and other high-melting transition metals. Such alloys must be purified from gases by vacuum annealing at temperatures as high as possible after or before melting. High-vacuum annealing before melting is always necessary, when mixed and pressed powders are melted. These often have high gas contents, which cause sputtering during arc melting. The melted specimens are turned over after a first melting, and are then remelted, because a single melting does not ensure complete mixing.

High-temperature annealing should be done in high vacuum or in purified argon.

We normally combine sintering and melting, using a tungsten arc furnace and an atmosphere of purest argon. In Figs. 4–6 the apparatus used in our metallurgical laboratory is shown. Fig. 4 shows a high-vacuum apparatus, which can be used for

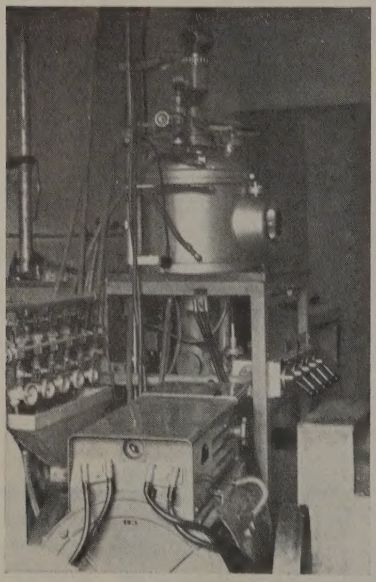

Fig. 4. Vacuum furnace (W. C. Heraeus, Hanau), tungsten arc-melting, sintering and resistance heating.

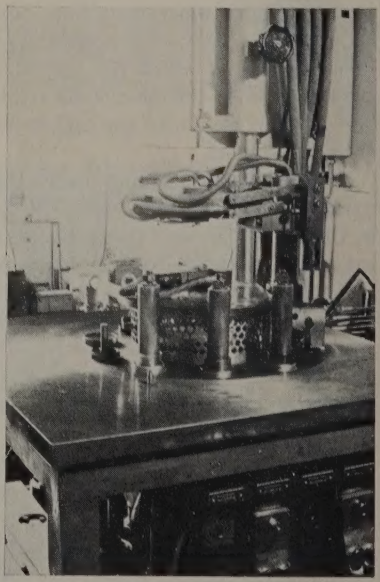

Fig. 5. Furnace shown in Fig. 4, with recipient removed, showing the arrangement for resistance-annealing and sintering.

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tungsten arc melting, as well as for sintering and annealing. In Fig. 5 the apparatus is shown with the cover removed in order to expose the sintering and annealing arrangement. Fig. 6 shows the so-called button furnace, whose name is derived from the form of the melted specimens. It is a tungsten arc furnace, in which eleven test pieces can be melted at one loading.

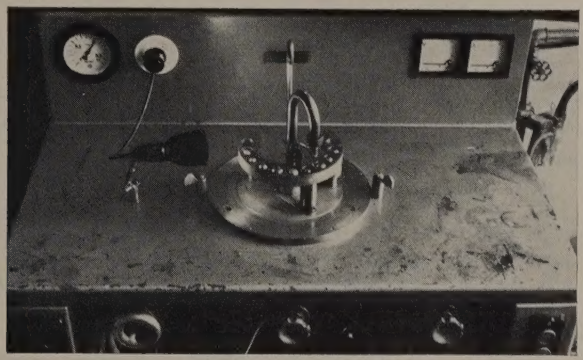

Fig. 6. Button furnace (Degussa, Hanau), tungsten arc furnace, without recipient.

STRUCTURE OF BINARY ALLOYS

We shall now consider briefly the structure of the binary alloys of the platinum metals with one another, and with other high-melting metals. The main difficulties of such investigations are often the impossibility of reaching the equilibrium state, and the existence of high-temperature phases which may be easily overlooked. Contamination or changes in the composition at high temperatures may also escape observation.

Table I shows the position of the platinum metals with the adjacent metals in the Periodic System. While among the other metals polymorphic transformations are common, the platinum metals exist only in one modification; for ruthenium this is not absolutely certain. Four of the platinum metals crystallize in the face-centered cubic structure. Ruthenium and osmium, together with technetium and rhenium are close-packed hexagonal. Among the other metals of Group VIII and VII, at least one modification is f.c. cubic. The high-melting metals from the VIA to the IVA Group crystallize in the body-centred cubic structure, or when more than one modification exists, at least one of them is b.c. cubic.

Alloys of the platinum metals with one another

The alloys of the four f.c.c. platinum metals with one another appeared of little scientific interest, because it was generally assumed that these alloys formed unbroken series of solid solutions. There were, however, indications that in the case of the platinum–iridium alloys the primary solid solutions were not stable at low temperatures[6,7].

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TABLE I

ATOMIC AND CRYSTAL STRUCTURE OF THE PLATINUM METALS AND THE ADJACENT METALS

22 Ti $3d^2\ 4s^2$ β ○ α ⬭	23 V $3d^3\ 4s^2$ ○	24 Cr $3d^5\ 4s^1$?β □ α ○	25 Mn $3d^5\ 4s^2$ δ ○ γ □ β compl. α compl.	26 Fe $3d^6\ 4s^2$ δ ○ γ □ α ○	27 Co $3d^7\ 4s^2$ β □ α ⬭	28 Ni $3d^8\ 4s^2$ □	29 Cu $3d^{10}\ 4s^1$ □
40 Zr $4d^2\ 5s^2$ β ○ α ⬭	41 Nb $4d^4\ 5s^1$ ○	42 Mo $4d^5\ 5s^1$ ○	43 Tc $4d^6\ 5s^1$ ⬭	44 Ru $4d^7\ 5s^1$ ⬭	55 Rh $4d^8\ 5s^1$ □	46 Pd $4d^{10}$ – □	47 Ag $4d^{10}\ 5s^1$ □
72 Hf $5d^2\ 6s^2$ β ○ α ⬭	73 Ta $5d^3\ 6s^2$ ○	74 W $5d^4\ 6s^2$ α ○ +)	75 Re $5d^5\ 6s^2$ ⬭	76 Os $5d^6\ 6s^2$ ⬭	77 Ir $5d^7\ 6s^2$ □	78 Pt $5d^8\ 6s^2$ □	79 Au $5d^{10}\ 6s^1$ □

+) β-W cube complex in presence of oxygen □ f.c. cubic ○ b.c. cubic ⬭ c.p. hex.

Fig. 7 shows the lattice constants of these alloys after high-temperature annealing. It can be seen that they have a continuous slope, which nearly agrees with Vegard's law. All curves confirm that there is unbroken miscibility in all the binary alloys of the f.c.c. platinum metals with one another at high temperatures. A thorough study

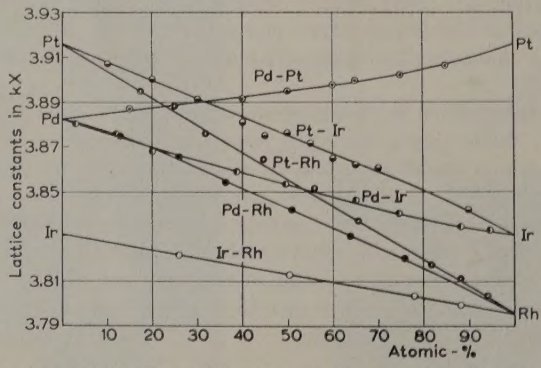

Fig. 7. Lattice constants of the alloys of the f.c.c. platinum metals with one another after high-temperature annealing.

of the properties at different temperatures showed, however, the existence of a wide miscibility gap in the palladium–iridium[8], palladium–rhodium[9] and platinum–iridium[10] alloys, as shown in Fig. 8.

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In these alloys the thermodynamical equilibrium state is reached very slowly. Even after an annealing time of more than one year, true equilibrium does not result, especially in the platinum–iridium system. Therefore, the limits of the miscibility gap cannot be measured exactly, but the critical temperatures show great differences.

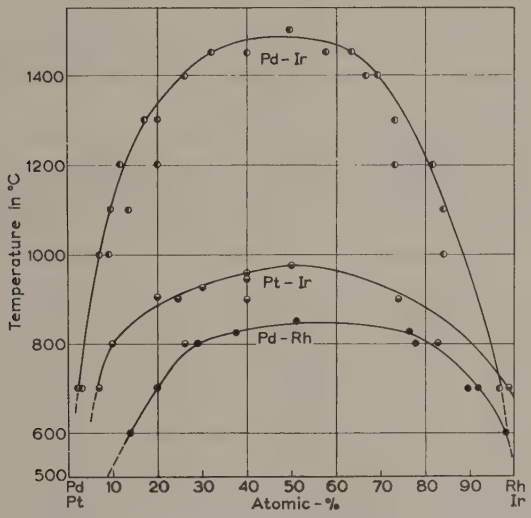

Fig. 8. Miscibility gaps of the alloys of f.c.c. platinum metals at lower temperatures.

It seems certain that, in the platinum–rhodium, platinum–palladium, and rhodium–iridium alloys, similar miscibility gaps exist at lower temperatures, but have not yet been observed.

Table II shows several of the properties of the f.c.c. platinum metals. The atomic radii and the lattice constants show only small differences, which cannot be the reason for differences in the critical temperatures of the miscibility gaps, but on considering

TABLE II

PROPERTIES OF THE F.C.C. PLATINUM METALS

Metal	*Atomic radii in kX*	*Lattice constant in kX*	*Melting point in °C*
Rh	1.34	3.797	1960
Pd	1.37	3.883	1554
Ir	1.35	3.831	2454
Pt	1.38	3.916	1769.9

the melting points of the pure metals, and comparing them with the critical temperatures of the miscibility gaps, a distinct relation is seen, as is shown in Table III.

TABLE III

DIFFERENCE IN THE MELTING POINTS OF THE F.C.C. PLATINUM METALS AND CRITICAL TEMPERATURE OF THE MISCIBILITY GAP

System	*Difference in the melting points in °C*	*Critical temperature of the miscibility gap in °C*
Rh–Pd	406	830
Rh–Ir	494	unknown
Rh–Pt	190	unknown
Pd–Ir	900	1476
Pd–Pt	216	unknown
Ir–Pt	684	975

components. In cases where miscibility gaps have not been observed, the melting points of the two metals do not differ greatly. Fig. 9 shows the ratio of the critical

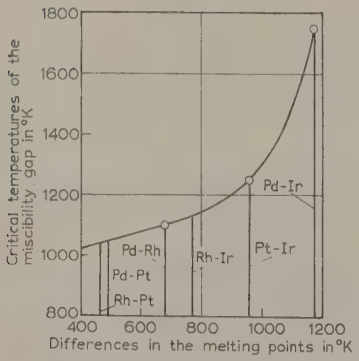

Fig. 9. Change of the critical temperature of the miscibility gap in f.c.c. platinum metals alloys with the temperature difference in the melting points.

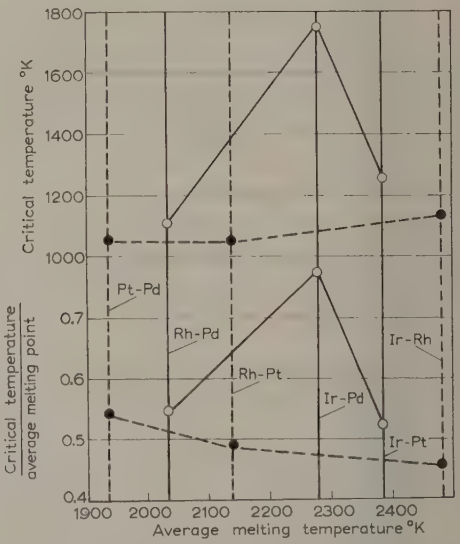

Fig. 10. Critical temperature of the miscibility gap in the alloys of f.c.c. platinum metals and average melting temperature.

temperature to the difference in the melting points. The curve shows a rapid decrease in the critical temperature with falling difference in the melting points. From this curve one may extrapolate a possible critical temperature for the miscibility gaps of the rhodium–iridium, palladium–platinum and platinum–rhodium alloys. Fig. 10 shows the average melting points of the alloys, and the experimentally found temperatures of the miscibility gaps or those estimated by extrapolation. It can be seen that miscibility gaps have been found in the alloys where the expected conditions are most favourable.

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According to Fig. 10, the experimental proof of the miscibility gap in the platinum–palladium alloys should be possible, but it is to be expected that the attainment of the equilibrium state will meet the same difficulties as in the platinum–iridium alloys. Indications of a miscibility gap in the platinum–palladium alloys have already been observed by BEESKOW. But a very prolonged heat treatment will be necessary before sufficiently exact measurements can be made. In the iridium–rhodium alloys, the conditions for the experimental proof of a miscibility gap are most unfavourable, because here the ratio of the critical temperature to the melting interval of the alloys is very low. For the rhodium–platinum alloys the experimental proof will also be very difficult.

Fig. 11 shows the lattice constants of the ruthenium–osmium alloys. At high temperatures the two metals form – as expected – an unbroken series of solid solutions. The formation of a miscibility gap in the solid state at lower temperatures could not be observed, but the conditions are unfavourable for the proof of a precipitation at lower temperatures.

Alloys of platinum metals with one c.p. hexagonal component

The structures of the alloys of the c.p. hexagonal metals with the f.c.c. platinum metals are only very incompletely known, although some of these alloys are of technical interest. In these alloys the atomic size factor is favourable for solid solutions. As the two metals crystallize in different lattices, we may expect a two-phase field, and this is confirmed by such experimental work as has been carried out.

HELLAWELL AND HUME-ROTHERY[11] determined the lattice constants of dilute solid solutions of rhodium and palladium in ruthenium. NEMILOV AND RUDNIZKY[12], and AGEEV AND KUZNETSOV[13] observed a solubility of about 70 at.-% Ru in platinum.

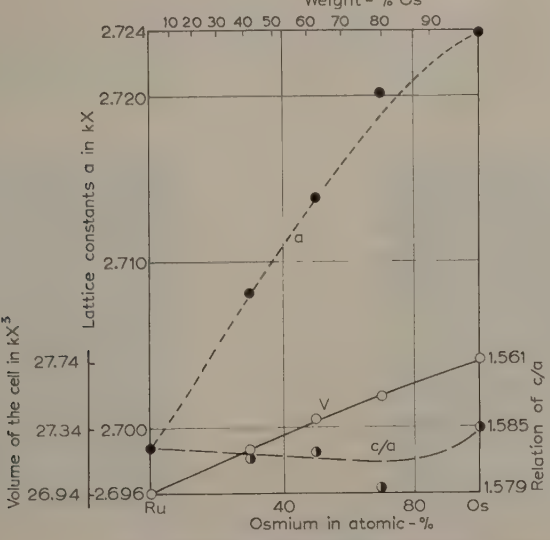

Fig. 11. Lattice constants of the ruthenium–osmium alloys.

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The exact measurement of the limits of the solid solutions in these alloys is very difficult, because the equilibrium state can seldom be obtained.

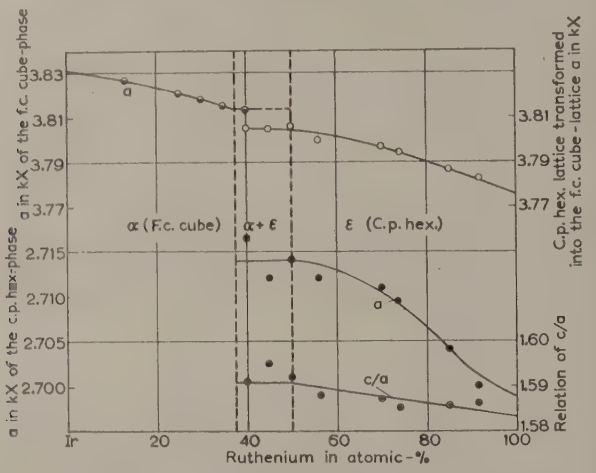

Fig. 12. Lattice and lattice constants of the iridium–ruthenium alloys.

In Fig. 12 the results of X-ray studies of the iridium–ruthenium alloys are given. According to these results the miscibility gap is only small and extends from about 37.5 to 50 at.-% ruthenium[11]. Between 1300 and 800°C no change of the lattice constants was observed, but it is not improbable that this result is due to incomplete equilibrium. The equilibrium diagram of iridium–ruthenium alloys has not yet been completely investigated; X-ray studies and microscopical investigations indicate that there is a transformation in the solid state near the saturation limit of the c.p. hexagonal phase, as shown by Fig. 13 for an alloy with 55 at.-% Ru.

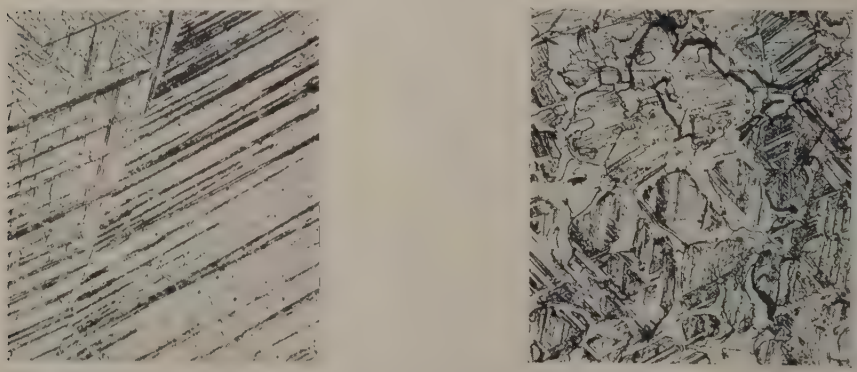

Fig. 13. Iridium–ruthenium alloy with 55 at.-% Ru. Left: slowly furnace cooled (× 200); right: quenched after 10 h heat treatment at 1000°C (× 200).

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In the two-phase field the crystallization is probably peritectic, as may be expected for alloys of ruthenium, osmium and rhenium with the f.c.c. platinum metals and with the f.c.c. iron metals. Most of the latter alloys have been very incompletely investigated. Fig. 14 shows a schematic diagram of several of these alloys. The alloys

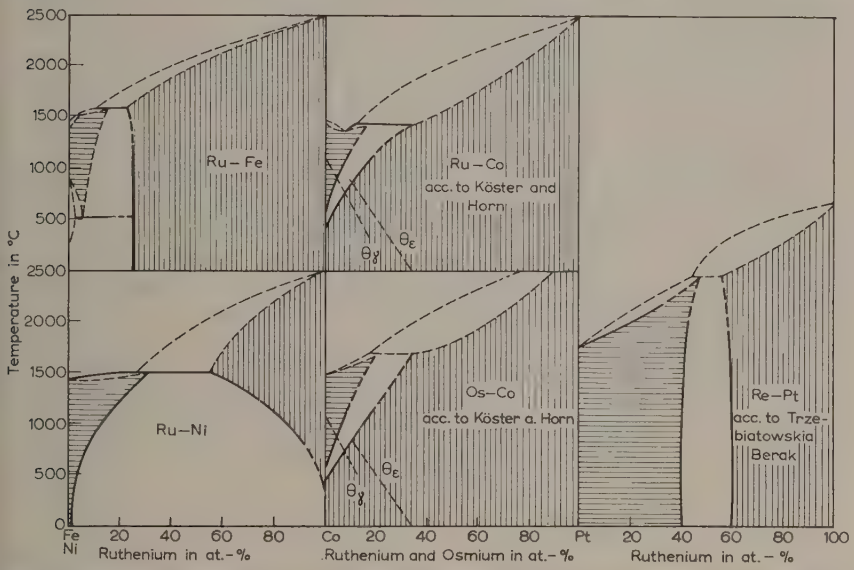

Fig. 14. Schematic diagram of several alloys of platinum metals with one c.p. hex. component.

of the platinum metals with cobalt were investigated by KÖSTER AND HORN[15]. The rhenium–platinum system is given according to an investigation of TRZEBIATOWSKI AND BERAK[16]. The ruthenium–iron and ruthenium–nickel diagrams are drawn according to our own unpublished investigation. The figure gives only a schematic picture of these systems and may be incorrect in some respects. The alloys shown in Fig. 14 have a two-phase field between the c.p. hexagonal and the f.c.cubic phase. It may be pointed out that the c.p. hexagonal solid solutions exist in places over a long range of composition. In the ruthenium–nickel alloys, the temperature dependence of the solution limits is of some interest.

The precipitation hardening curves of two nickel–ruthenium alloys, given in Fig. 15, show after an initial rise a decrease of hardness, and after a certain time the hardness increases again, thus forming two peaks. This is the result of the so-called cold and hot aging phenomenon and is observed best at an annealing temperature of 150°C, but with short annealing times it can also be seen at 300 and 500°C.

Alloys of the f.c.c. platinum metals with the f.c.c. modifications of iron, cobalt and nickel

As known at present the four f.c.c. platinum metals form unbroken solid solutions with the f.c.c. modifications of iron, cobalt and nickel[17]. In many of the alloys of f.c.c. platinum metals with iron, cobalt and nickel there are transformations, especially of the CuAu and Cu_3Au types. Unpublished investigations by ourselves and

BEESKOW showed the existence of a series of unbroken solid solutions in the rhodium–nickel alloys, and in the alloys of rhodium with γ-iron. In the rhodium–iron alloys, an ordered phase of the composition FeRh with a b.c.c. lattice was found, in agreement with the indications of FALLOT AND HOCART[18]. In the nickel–rhodium alloys, a transformation occurs at temperatures below about 500°C, by which an ordered structure of the Cu_3Au type is formed.

The alloys of the platinum metals with iron, cobalt and nickel are also of interest for their magnetic properties, and research work is being carried out on this subject.

Alloys of platinum metals with manganese

In this connection, the alloys of the platinum metals with manganese are also of interest. In alloys of the f.c.c. platinum metals with manganese, a β-phase of the CsCl type exists. But only in the rhodium–manganese alloys does this phase suffer no transformation at lower temperatures[19]. The platinum–manganese alloys have an ordered structure of the Cu_3Au type, which is ferromagnetic. Ferromagnetism and, obviously, also antiferromagnetism were to some extent observed in the β-fields[20]. The influence of the platinum metals on the modifications of manganese is also of interest, and results are shown in Fig. 16. The f.c.c. γ-phase is expanded by the platinum metals down to room temperature, except in palladium–manganese alloys where the γ-manganese solid solution decomposes eutectoidally. In the rhodium, iridium and platinum alloys the γ-phase shows a transformation of the Cu_3Au type.

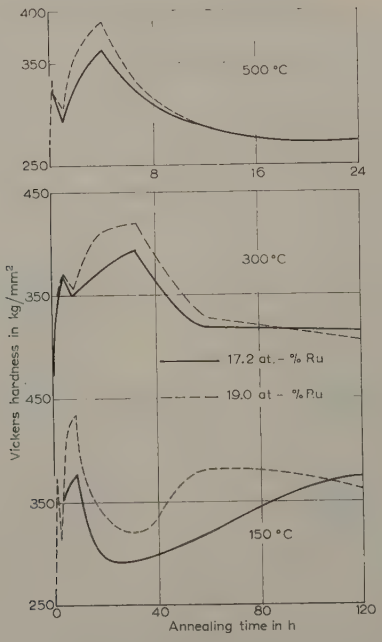

Fig. 15. Precipitation hardening of nickel–ruthenium solid solutions.

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Alloys with a content of platinum metals at which the β- and α-form of manganese still exist, show not only the tetragonal form of γ-manganese with a c/a ratio less than 1, which is formed on quenching, but also a second form of γ-manganese with a c/a ratio of more than 1, which is also formed by quenching.

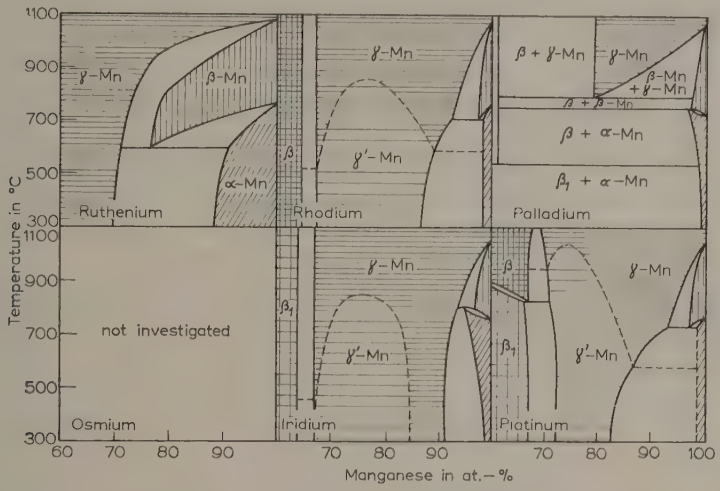

Fig. 16. The influence of platinum metals on the transformations of manganese.

Alloys of platinum metals with metals of Group VIA

Interesting relations exist in the alloys of the Group VIA metals with platinum metals. Fig. 17 shows the phasefields existing in these alloys at temperatures below about 1600°C. It can be seen that according to HUME-ROTHERY's rule, the solid solution in the metals with the lower coordination number is much more restricted than that

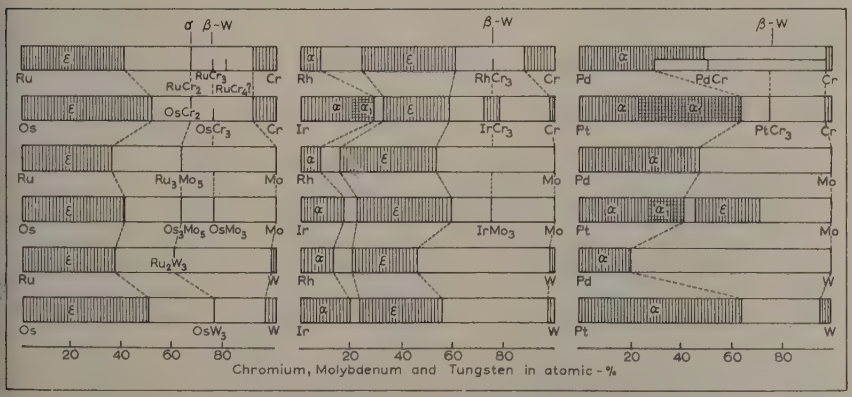

Fig. 17. The alloys of platinum metals with the metals of the VIA Group.

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in the metals with the higher coordination number. Furthermore, the existence of the tetragonal phase σ in all alloys of the c.p. hexagonal platinum metals with the VIA metals is of interest. In these alloys the σ-phase has the typical properties which it was already found to possess in other alloys. It often exists only at high temperatures, and for this reason it was not found in GREENFIELD AND BECK'S[25] and our own research[21] on the ruthenium tungsten alloys, but OBROWSKI[29] detected its existence at temperatures above 1750°C.

The σ-phase is always distinguished by an extremely high hardness and brittleness. In three of the alloys of the c.p. hexagonal platinum metals with the VIA metals there exists the β-W-phase at the compositions $RuCr_3$, $OsCr_3$ and $OsMo_3$. In the rhodium and iridium alloys the existence of a c.p. hexagonal phase with a wide field of homogeneity is remarkable; the composition changes to a certain extent from alloy to alloy, but always lies between about 20 and 60 at.-%.

We see that by alloying the b.c.c. metals of Group VIA with the f.c.c. platinum metals immediately adjacent to the c.p. hexagonal metals of Group VII and VIII, an intermediate phase with the c.p. hexagonal structure of the last is formed. Considering the f.c.c. metals which have an atomic number one unit higher, namely palladium and platinum, the tendency to form the c.p. hexagonal intermediate phase is smaller, and this phase is found only in the platinum–molybdenum alloys.

The β-W-phase was found in chromium and molybdenum alloys of iridium, and in the platinum–chromium alloys. σ-phases were discovered by KNAPTON[30] as high-temperature phases in the alloys of iridium with molybdenum and tungsten. Ordered phases were observed in the f.c.c. solid solutions of iridium–chromium, platinum–chronium and platinum–molybdenum*. In the palladium chromium alloys a tetra-

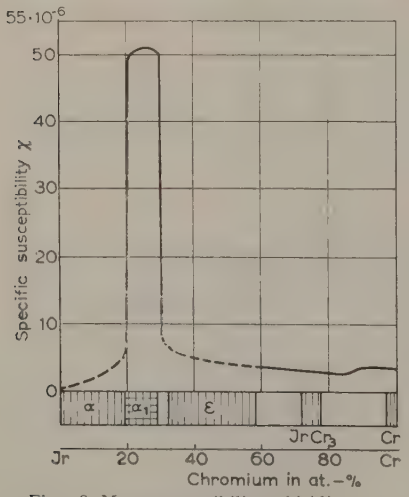

Fig. 18. Mass-susceptibility of iridium–chromium alloys.

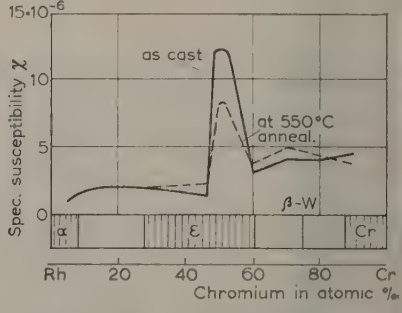

Fig. 19. Mass-susceptibility of rhodium–chromium alloys.

* According to V. A. NEMILOV AND A. A. RUDNITSKII (*Izvest. Sektora Platiny*, 21 (1948) 234 ref. M. HANSEN AND K. ANDERKO, *Constitution of Binary Alloys*, McGraw-Hill Book Co., Inc. New York, 1958, p. 1145) there are also indications of the existence of an ordered phase in the platinum–tungsten alloys at 25 at.-% W.

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gonal phase PdCr is formed by peritectoid reaction at low temperatures. In some of these alloys ferromagnetism was observed[31]. Fig. 18 shows the specific susceptibility of chromium–iridium alloys; the ordered α_1-phase is ferromagnetic, and the specific susceptibility reaches about $50 \cdot 10^{-6}$. In Fig. 19 results of magnetic measurements on rhodium–chromium alloys are reproduced. In these alloys the c.p. hexagonal phase shows ferromagnetic properties. The specific susceptibility rises to a value of about $12 \cdot 10^{-6}$.

Alloys of platinum metals with metals of Groups VA and IVA

The alloys of platinum metals with the metals of the VA and IVA Group have only been partially investigated. Even so, it is possible to see several relations between these alloys. HELLAWELL AND HUME-ROTHERY[11] measured the lattice spacings of

TABLE IV

INTERMEDIATE PHASES IN THE ALLOYS OF PLATINUM METALS WITH GROUP IVA AND VA METALS According to LAVES AND WALLBAUM[32], WALLBAUM[33], GELLER[34], GREENFIELD AND BECK[25], KNAPTON[30], GELLER, MATTHIAS AND GOLDSTEIN[35]

Alloy	*Intermediate phase*				*Other phases*
	σ	β-*W* *A 15*	*CsCl* *B 2*	*Laves* *C 14*	
Ru–Ti			TiRu		
Zr			ZrRu	$ZrRu_2$	
V			64 at. % V		VRu tetr. and unidentified phase
Nb			68 at. % Nb		NbRu tetr. ?, probably 2 further phases
Ta			62 at. % Ta		TaRu tetr. ?
Os–Ti			TiOs		
Zr				$ZrOs_2$	
V					Unidentified phases
Nb	Nb_3Os_2	Nb_3Os			Cub. α-Mn
Ta	25–50 at.-% Os				Cub. α-Mn
Rh–V		V_3Rh			At 60 at.-% Rh c.p. hex.
Nb	Nb_3Rh_2	Nb_3Rh			Further phases probable
Ta	Ta_3Rh_2				Further phases probable
Pd–Ni					$TiPd_3$ DO_{24} type Ti_2Pd_3 unknown
					Ti_2Pd isotype Ti_2Ni
V					Probably phase of unknown structure
Nb	Nb_3Pd_2				
Ir–Ti		Ti_3Ir			
Zr				$ZrIr_2$	
V		V_3Ir			Unidentified phase
Nb	35 at. -% Ir	Nb_3Ir			Unidentified phase
Ta	Ta_3Ir				Unidentified phase
Pt–Ti		Ti_3Pt			$TiPt_3$ L l_2, Ti_2Pt_3 unknown
					Ti_2Pt isotype Ti_2Ni
Zr					$ZrPt_3$ DO_{24} type
V		V_3Pt			A further phase probable
Nb	Nb_5Pt_3	Nb_3Pt			
Ta	Ta_3Pt				Further phase at 57–65 at.-% Ta unidentified

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several dilute solid solutions. Measurements of saturation limits of the primary solid solutions have not been published; only approximate data are to be found. Table IV gives a survey of the intermediate phases. In ruthenium alloys the CsCl structure is predominant, and there is, in addition, a tetragonal structure. As far as known at present only in two cases, namely the osmium–tantalum and osmium–niobium alloys, does a σ-structure exist, although this structure was found in all the alloys of the c.p. hexagonal platinum metals with those of the VA Group. It is remarkable that the σ-phase is found in many of the alloys of the f.c.c. platinum metals, whilst obviously it exists in only a few alloys of these platinum metals with those of the VIA Group.

In the alloys of the f.c.c. metals with metals of Groups IVA and VA we also often find the β-W-phase, and other intermediate crystal structures also exist. In three alloys the presence of Laves-phases has been proved, and in one series of alloys there are intermediate phases, which could not be identified.

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TUNGSTEN ALLOYS OF HIGH MELTING POINT

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Tungsten is the metal with the highest melting point, and among the elements it ranks second only to carbon. Only a few metallic compounds, namely the monocarbides of zirconium, hafnium, niobium, and tantalum have higher melting points than tungsten.

A survey of the literature in connection with the 100th anniversary of the birth of K. AUER VON WELSBACH shows that only seventy years ago this famous Austrian scientist and inventor regarded osmium as the metal with the highest melting point, since it was thought that tantalum and tungsten melted at 2300°C and 2500°C respectively. It was for this reason that VON WELSBACH developed the osmium lamp which, as he freely admits[1], prevented him from attaining the financial success which would have been achieved if he had used tantalum or tungsten.

In the Periodic Table, the high-melting metals are found in the Groups of the transition metals (T metals). These possess abnormally high binding energies, which exceed the energies normally associated with metallic bonding. It is supposed that this higher binding energy is connected with the number of *d* electrons concerned[2], and that the melting points of the metals rise with stronger bonding in the crystal structure. On proceeding along the horizontal rows of the Periodic Table, the number of *d* electrons in the transition metals increases from 1 to 10. The binding energy produced by these *d* electrons is regarded as approaching a maximum at 5 *d* electrons, after which it decreases as the number of *d* electrons increases from 6 to 10. According to this view, chromium, molybdenum, and tungsten possess 5 *d* electrons, and have the highest binding energies, and highest melting points in each horizontal row of the Periodic Table.

Fig. 1, according to W. EPPRECHT, shows the relation between the number of *d* electrons and the position of the metals in the Periodic Table as well as the periodic change of the melting point. On the right are compared the melting points of non-metals, oxides, and of some materials of great hardness.

The melting point of tungsten is not raised by alloying with 50 at.-% carbon or 66.7 at.-% boron, and no carbide or boride of tungsten has a higher melting point than the pure metal. This is in contrast to the behaviour of the T metals of Groups IVA and VA when alloyed with boron and carbon.

When tungsten is alloyed with metals of Groups IVA–VIIIA one finds either complete miscibility, or as in the case of W–Re, formation of intermetallic compounds of lower melting point than pure tungsten.

Fig. 2 shows the melting points and crystal structures of the transition metals with which we are concerned, as well as the type of equilibrium diagram. Tungsten shows

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complete miscibility with niobium, tantalum, and molybdenum; with chromium there is a miscibility gap at low temperatures, but complete miscibility at high temperatures. The equilibrium relation of tungsten and vanadium resembles those of Mo–V[6]. The metals of Groups IVA, VIIA and VIIIA form restricted solid solutions in tungsten, as shown by the vertical lines in Fig. 2.

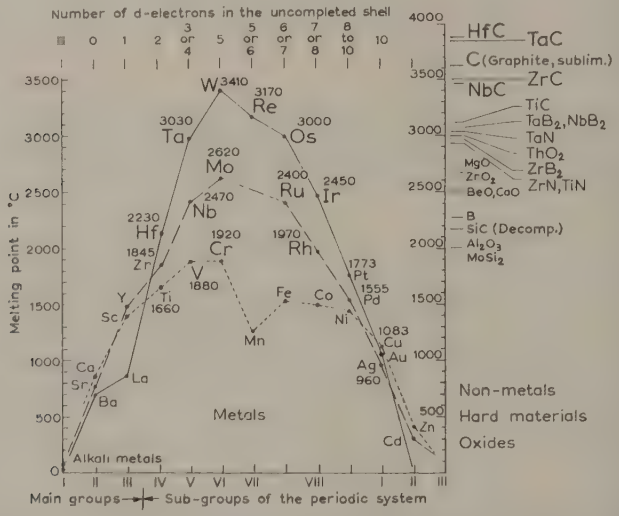

Fig. 1. Melting points of metals and their position in the Periodic Table of the elements (according to W. Epprecht).

IVa	Va	VIa	VII a	VIII a	
22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co
m.p. = 1660°	1885°	1890°			
40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh
m.p. = 1845°	2470°	2620°		2400°	1970°
72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir
m.p. = 2230°	3030°	3380°	3170°	3000°	2454°

⊙ = face-centred cubic A1
■ = body-centred cubic A2
⬡ = close-packed hexagonal A3
m.p. = melting point in °C

Fig. 2. Transition metals of Groups IVA, VA and VIA and their high-melting neighbours: crystal structure, melting point and type of constitutional diagram of alloy systems.

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Lattice parameter determinations by BÜCKLE[3] on alloys of Nb, Ta, Mo, and W have shown that HUME-ROTHERY's 15% rule is obeyed (Fig. 3). In dealing with high-melting tungsten alloys we have, therefore, concentrated on tungsten-rich alloys which are easily workable and have practical technical possibilities. Such alloys have been found by others, and their existence has been confirmed by our work on alloys from the systems W–Nb, W–Ta, W–Mo, and W–Re.

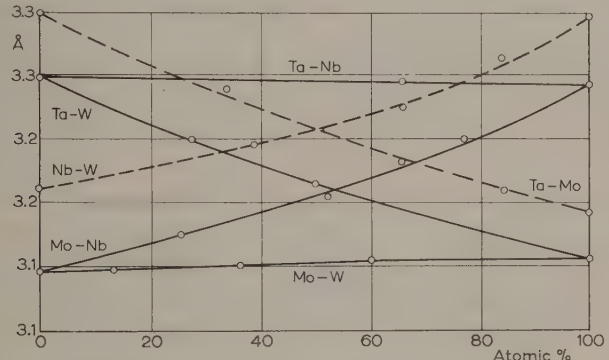

Fig. 3. Lattice parameters of alloys of the metals tungsten, niobium, tantalum and molybdenum[3].

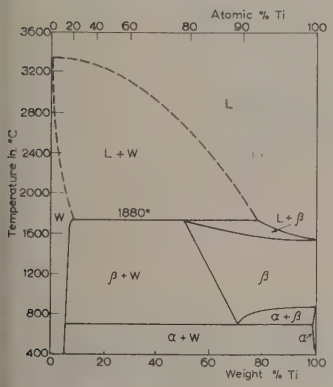

Fig. 4. Constitutional diagram of W–Ti[4].

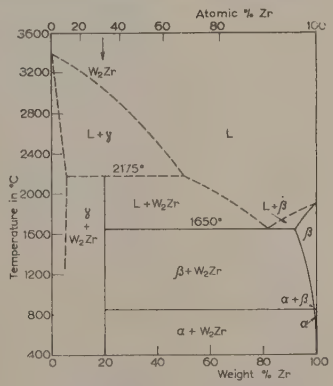

Fig. 5. Constitutional diagram of W–Zr[5].

I. ALLOYS OF TUNGSTEN WITH TITANIUM, ZIRCONIUM AND HAFNIUM

The solubility of titanium[4] and zirconium[5] in tungsten is small (Figs. 4 and 5). We have prepared small samples of W-rich alloys to investigate their hot-forgeability. The results are shown in Fig. 6. The only alloys to show some plasticity are the coarse-grained arc-cast alloys of less than 8% Ti, and the fine-grained sintered alloys with from 5 to 10% Ti. Tungsten–zirconium alloys show bad hot-workability over the entire range from 1 to 10% Zr. This is in good agreement with the work of PIPITZ AND KIEFFER[6] on the alloys of Mo with Ti and Zr.

The constitutional diagram of the system W–Hf has not been investigated as yet. It is expected to be only slightly different from the system W–Zr.

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II. ALLOYS OF TUNGSTEN WITH CHROMIUM AND MOLYBDENUM

Tungsten is completely miscible with chromium at temperatures above 1500°C; below this temperature there is a wide solubility gap[7] (see Fig. 7).

Qualitative work on coarse-grained arc-cast material indicates that bad workability is exhibited by tungsten-rich chromium alloys. The workability of fine-grained sintered W–Cr alloys is relatively high (Fig. 8).

Tungsten and molybdenum are completely miscible. The properties of mass-produced tungsten–molybdenum alloys are shown in Fig. 9. Ultimate tensile strength, yield strength, hardness and Young's modulus increase with higher W-contents, whereas the elongation decreases gradually from about 25 to 1(3)%. These alloys are unsatisfactory, and except for the elongation all the properties of tungsten deteriorate on the addition of molybdenum.

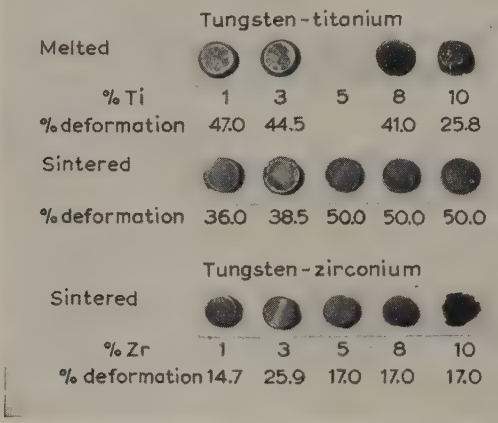

Fig. 6. Hot-workability of W–Ti and W–Zr alloys.

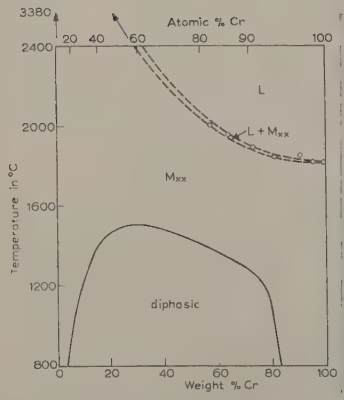

Fig. 7. Constitutional diagram of W–Cr[7].

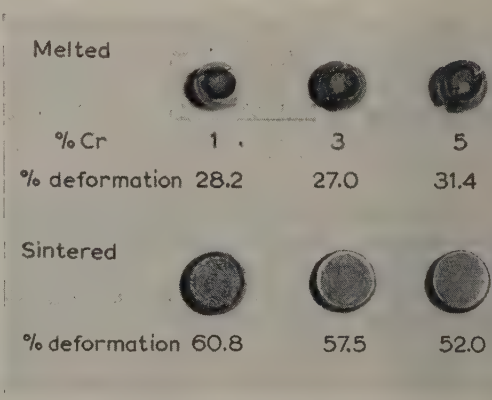

Fig. 8. Hot-workability of some W–Cr alloys

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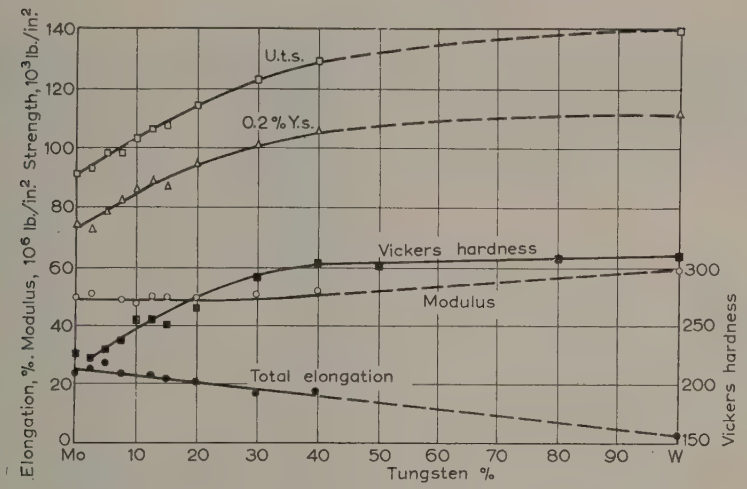

Fig. 9. Mechanical properties of W–Mo alloys at room temperature.

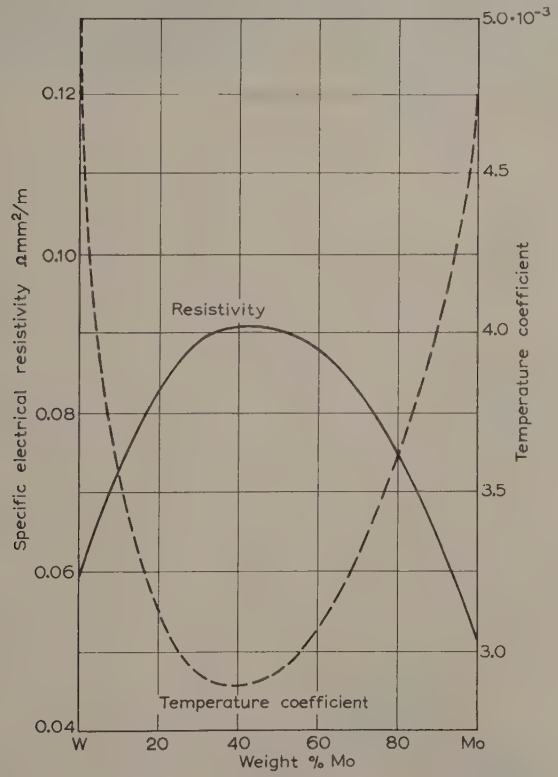

Fig. 10. Specific electrical resistivity of W–Mo alloys and its temperature coefficient.

Fig. 10 shows that the specific electrical resistivity of W–Mo alloys has a maximum at 50 wt.-% molybdenum; its temperature coefficient shows a minimum at the same composition. This is widely utilized in the lamp and radio-tube industry, where W–Mo alloys of the composition 50/50 are common as support wires of low conductivity. W–Mo alloys with 10% tungsten find extensive use in zinc die-casting equipment, because they show good corrosive resistance to molten zinc.

III. ALLOYS OF TUNGSTEN AND RHENIUM

For W–Re alloys we refer to the work of GEACH AND HUGHES[8], JAFFEE, SIMS AND HARWOOD[9] and SAVICKIJ AND TYLKINA[10].

The liquidus curve (Fig. 11) of the system tungsten–rhenium was first determined in 1930 by BECKER AND MOERS[11]. It agrees with the new curve obtained by SAVICKIJ AND TYLKINA[10], who give values for the microhardness that are in good agreement with those determined by JAFFEE *et al.*[9].

Fig. 12 indicates that α-solid solution alloys with 25 to 30% Re are more ductile at 1000°C than pure tungsten[9]. Fig. 13 shows the relationship between cold-ductility and rhenium-content for W–Re alloys as determined by GEACH AND HUGHES[8]. They found a maximum ductility at 30 to 35% Re. In Fig. 14 the high-temperature hardness of such alloys — which is excellent — is compared with that of pure tungsten, molybdenum, and Mo–Re alloys[8].

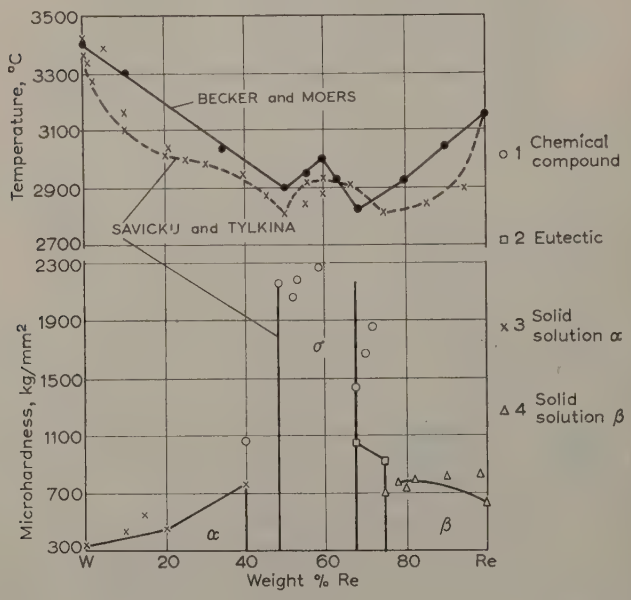

Fig. 11. Microhardness and liquidus curve in the system W–Re[10,11].

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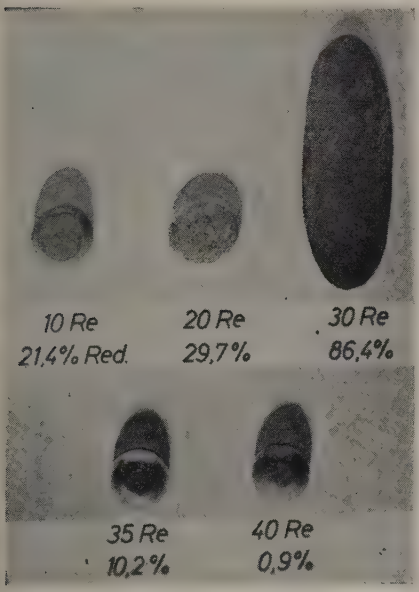

Fig. 12. Ductility of W–Re alloys at 1000°C[9].

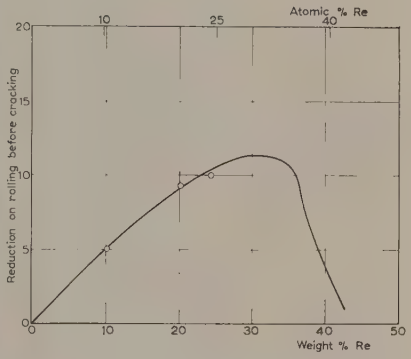

Fig. 13. Influence of rhenium on the cold-workability of tungsten[8].

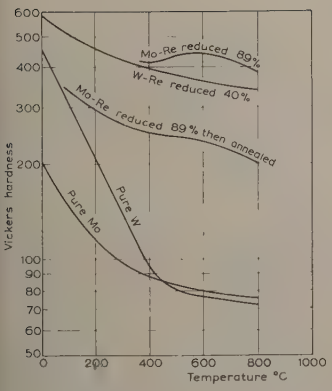

Fig. 14. Hot-hardness of some Re alloys[8].

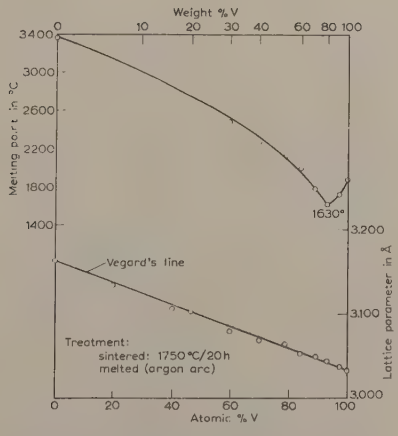

Fig. 15. Liquidus curve and lattice parameters in the system W–V.

IV. ALLOYS OF TUNGSTEN WITH PLATINUM-GROUP METALS

Investigations of tungsten alloys with osmium, rhodium, ruthenium, iridium, platinum, etc. have been carried out mainly on the noble metal sides of the systems[12,13]. The solubilities of platinum metals in tungsten, found in the literature, are low as shown by the following values:

Os in W	< 5 at.-%	[12]
Rh in W	< 2 at.-%	[12]
Ru in W	1.5 at.-%	[12]
Ir in W	2.5 at.-%	[12]
Pt in W	3.5–5.5 at.-%	[13]

GEACH *et al.*[14], who investigated Mo–Os alloys, found that these alloys have an appreciably higher cold-ductility than pure Mo; although this difference is much smaller than in the case of Mo–Re alloys, the behaviour of W–Os alloys might well be studied to see how they compare with the Mo–Os alloys in this respect.

V. ALLOYS OF TUNGSTEN WITH VANADIUM, NIOBIUM AND TANTALUM

According to PIPITZ AND KIEFFER[6] molybdenum and vanadium form a continuous series of solid solutions. From HUME-ROTHERY's 15% rule it may be supposed that this will also be true for the system W–V. ROSTOKER AND YAMAMOTO[15] have found that vanadium is capable of dissolving up to 40 wt.-% W. At higher concentrations of W they found two phases. We have determined the liquidus curve and lattice parameters for sintered and subsequently argon-arc melted specimens (Fig. 15). The melting point has a minimum at 80 wt.-% V and at 1630°C. The values for the lattice

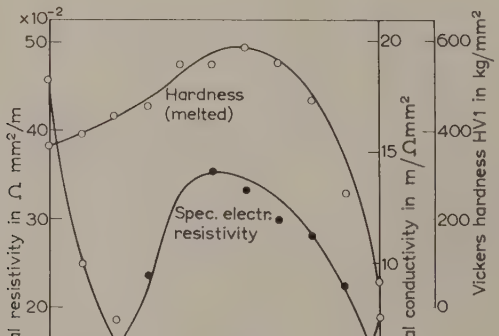

Fig. 16. Hardness, specific electrical resistivity and conductivity of W–Nb alloys.

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parameters for as-cast specimens are in good agreement with Vegard's law, which proves the complete miscibility of tungsten and vanadium at high temperatures.

Our latest investigations have shown that the equilibrium diagram in this system is similar to that of molybdenum–vanadium, exhibiting complete miscibility also at lower temperatures.

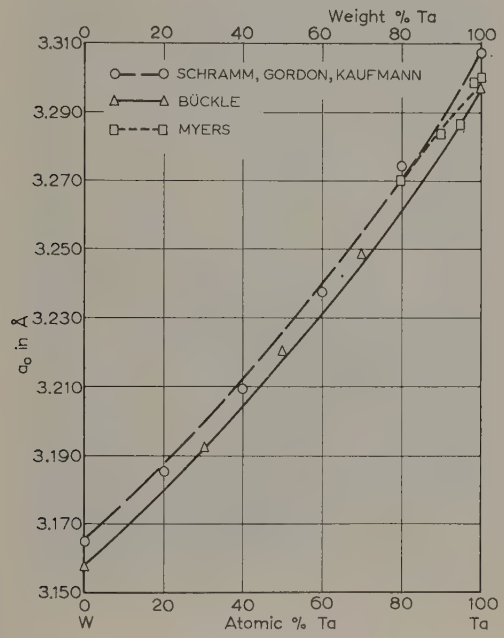

Fig. 17. Lattice parameters of W–Ta alloys.

Tungsten and niobium are completely miscible, as BÜCKLE[3] has already stated. With as-sintered as well as arc-cast specimens we have ascertained by means of hardness and conductivity measurements that there is complete miscibility of the two metals.

The hardness of tungsten niobium alloys (Fig. 16) shows a distinct maximum between 50 and 60 at.-% niobium. This is also true for the specific electrical resistivity, the specific electrical conductivity exhibiting the corresponding minimum, thus establishing the formation of a homogeneous solid solution from 0 to 100%.

That tungsten and tantalum are completely miscible was stated by V. BOLTON[16] in 1905. Proof of his non-empirical statement was given in 1946 by BÜCKLE[3], whose results were confirmed simultaneously by the X-ray work of SCHRAMM, GORDON AND KAUFMANN[17] and by MYERS[18] (see Fig. 17). Our own results are in good agreement with the values of BÜCKLE shown in Fig. 17. GEACH AND KNAPTON obtained similar results in investigations of the ternary system Mo–Ta–W (unpublished work, 1951).

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Investigations of the technological properties of tungsten–tantalum alloys have so far been restricted to either the W or Ta-rich ends of the system, since alloys of intermediate concentrations have been found to be unworkable under normal conditions. These difficulties induced us to concentrate on the entire range of alloys[19].

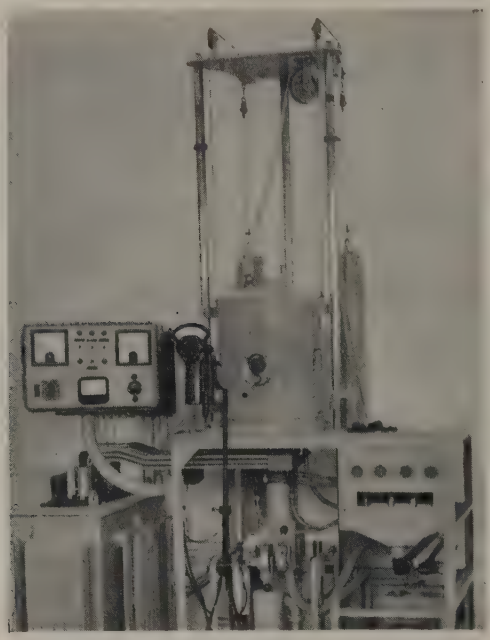

Fig. 18. Tungsten-tube high-vacuum furnace.

Sintering of the alloys

The first investigations of ALTSTETTER[20] in our laboratories in 1957 showed that a minimum of density occurs at an alloy 50/50 when W–Ta powder mixtures, pressed to bars with an average specific pressure of 6 t/cm², are directly sintered in vacuo. It is supposed that this widening of pores, giving rise to interconnection of cavities and a swelling of the specimens, is caused by a preferential diffusion of Ta into W, together with a certain getter effect of tantalum related to the evaporation of lower oxides. To overcome this, the specimens were prealloyed at 2300°C in a vacuum less than $6 \cdot 10^{-5}$ atm, thus producing an alloy powder for the final sintering at 2500 to 2600°C at vacua around 10^{-5} mm Hg.

This prealloying technique was carried out in a high-vacuum tungsten-tube furnace which is shown in Fig. 18.

The maximum power input of the furnace is 60 kW, allowing sintering temperatures of up to 2700°C at a vacuum of less than 10^{-5} atm. Fig. 19 shows how the tungsten tube is clamped between two water-cooled copper electrodes. The specimens are suspended in a tantalum carrier during sintering.

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After an 8-hours sintering of specimens pressed from alloy powder prepared by the method described above, the densities of the sintered parts approached values close to the theoretical density, in agreement with their mechanical and chemical properties.

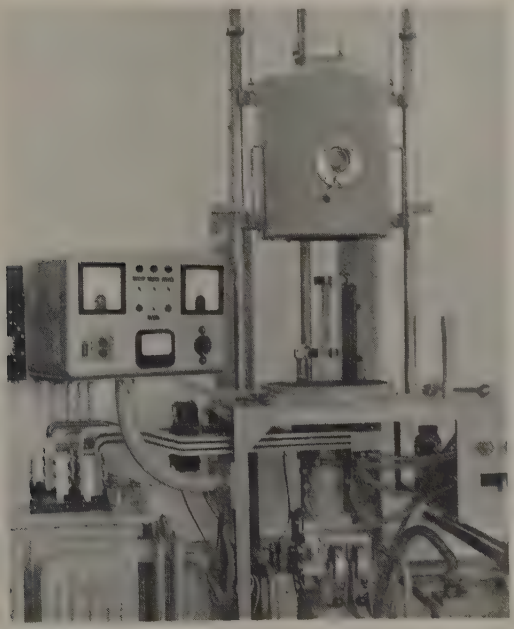

Fig. 19. Tungsten-tube high-vacuum furnace, installation of the tube.

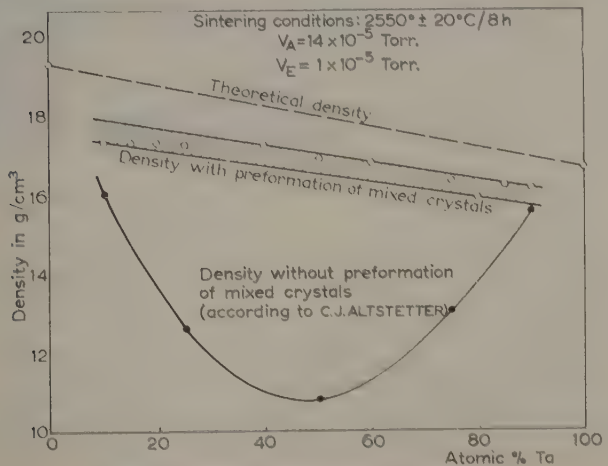

Fig. 20. Density of as-sintered W–Ta alloys.

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In Fig. 20 the curve with a minimum illustrates the variation of density with composition for specimens sintered once in a normal direct sintering bell. Above it is shown the effect of prealloying, giving values close to the theoretical density.

A study of the diffusion process in the system tungsten tantalum has been carried out in specimens 50/50 pressed from coarse-grain powder (0.1 0.2 mm) and sintered for different periods at various temperatures. We were able to show that minute deviations of the composition of W -Ta alloys change their electrochemical behaviour with respect to anodic oxidation (0.1 N H_3PO_4, 240 V, 2 10 min, 20 C), areas of different composition acquiring different colours.

Figs. 21–23 illustrate the diffusion process in W–Ta alloys.

Fig. 21 shows a specimen pressed from coarse-grain material after one-hour sintering at 1750 C. Anodic oxidation colours the tantalum blue, the tungsten grain appearing white. No diffusion has taken place.

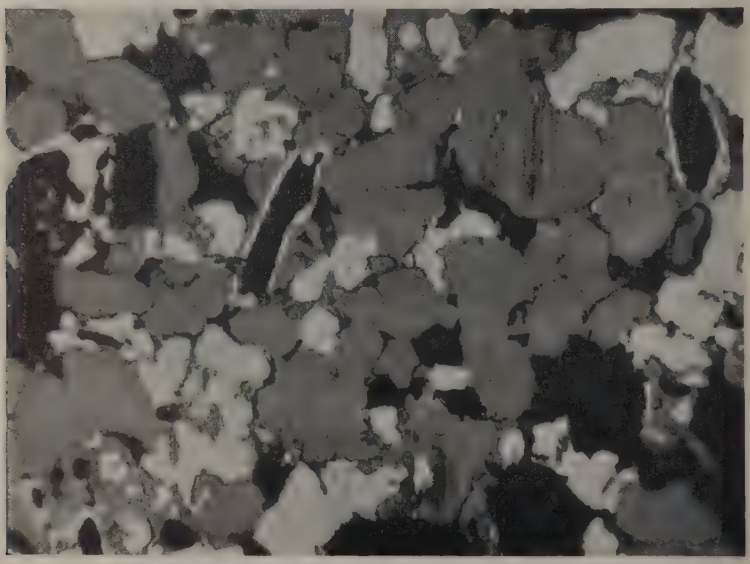

Fig. 21. W–Ta (50/50), 1750°C/1 h sintering (× 100).

Fig. 22 shows rapid diffusion starting after sintering for one hour at 2000°C. The tungsten grains, which appear bluish yellow are surrounded by a violet-coloured zone of an 80% tantalum–20% tungsten alloy with a microhardness of approximately 240 kg/mm².

A homogeneous solid solution with a microhardness of 480 kg/mm² is produced by sintering for ten hours or longer at 2600°C (Fig. 23).

Apparently the formation of solid solutions in the system tungsten–tantalum is achieved mainly through surface diffusion with subsequent lattice diffusion. Complete homogeneity is reached with sintering periods of not less than 12 15 hours at 2600°C

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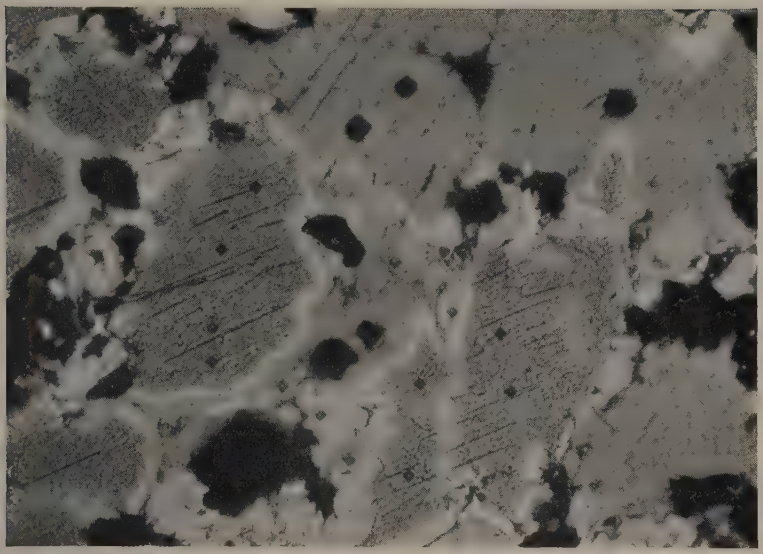

Fig. 22. W Ta (50/50), 2000°C/1 h sintering (× 200).

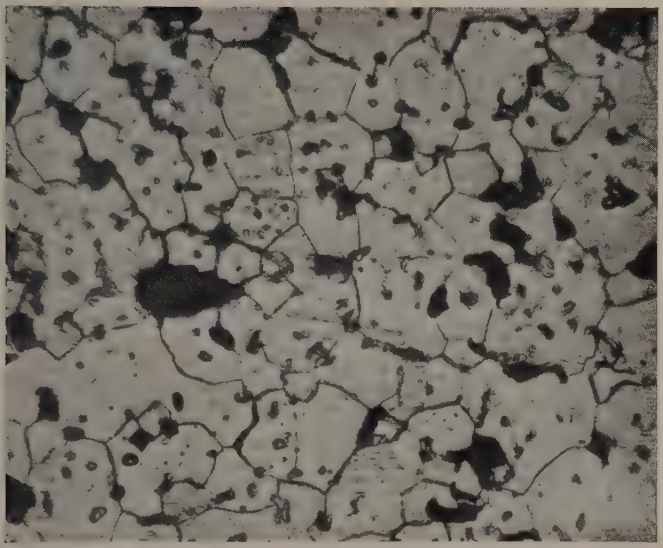

Fig. 23. W–Ta (50/50), 2600°C/10 h sintering, etching: fused KOH (× 400).

Properties of as-sintered alloys

In Fig. 24 the hardness of sintered as well as argon-arc cast alloys shows a distinct maximum. This maximum confirms KURNAKOW's views on binary alloys exhibiting complete miscibility. The minimum curve again demonstrates the high porosity of alloys prepared without pre-sintering.

A similar maximum as exhibited by the hardness is shown by the specific electrical

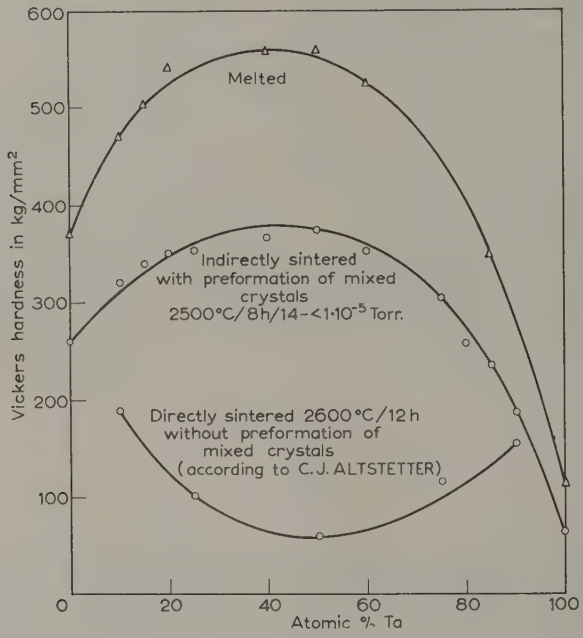

Fig. 24. Hardness of W–Ta alloys.

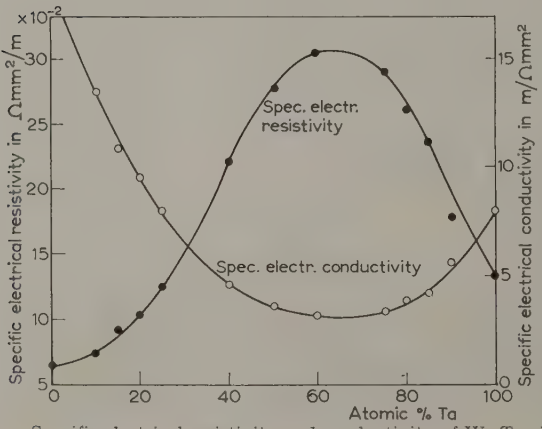

Fig. 25. Specific electrical resistivity and conductivity of W–Ta alloys.

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resistivity in Fig. 25, the conductivity showing the corresponding minimum. The maximum of the specific electrical resistivity is found with about 40% tungsten and is 30 $\mu\Omega$ cm.

Fig. 26 shows the corrosion rate of tungsten–tantalum alloys after treatment with aqueous solutions of KOH, $K_3Fe(CN)_6$ and HF. The two upper curves illustrate that a minimum corrosion rate is observed for 50/50 alloys when treated with either cold or hot potassium hydroxide. The corrosion in potassium ferricyanide diminishes gradually with rising tantalum contents.

No corrosion occurs when alloys of tantalum containing more than 15% of tungsten are submitted to the action of hydrofluoric acid.

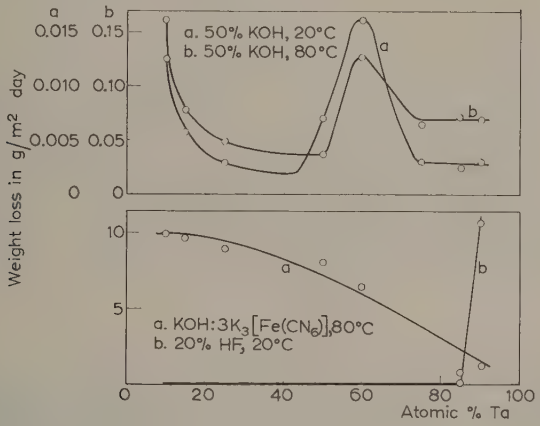

Fig. 26. Corrosion rate of W–Ta alloys.

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FACTORS AFFECTING THE GRAIN STRUCTURE OF AS-CAST MOLYBDENUM INGOTS

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INTRODUCTION

For many years the production of sound castings of the commoner metals by conventional methods has been largely a matter of trial and error[1]. In contrast, the vacuum and the inert-gas arc-melting processes are only about ten years old and the metals melted are usually the less commoner ones and are fairly expensive. In consequence, melting techniques are being developed on a scientific and experimental basis. Although this paper deals principally with molybdenum ingots produced by the cold-mould consumable-electrode arc-melting process, some of the principles of the results given should also be applicable to other metals.

THE CONSUMABLE-ELECTRODE ARC-MELTING PROCESS

The type of arc-melting equipment used for the studies reported in this paper is similar to that described by HOPKIN *et al.*[2]. Their paper covers not only the furnace design and its operation but also the metallurgical aspects of molybdenum and its alloys. MOSS[3] has discussed, in detail, the electrical characteristics of the molybdenum-depositing arc and of the arc-melting process. These two papers are, therefore, concomitant with, and provide a background for, this present paper.

In the consumable-electrode arc-melting process the metal to be melted is obtained in the form of a rod, which may be made by the powder-metallurgy technique and is contained in a chamber either under high vacuum or filled with an inert gas. The rod is connected to a source of alternating or direct current and is fed down centrally inside a water-cooled copper mould at the base of which is a disc of similar material forming the other electrode. When the two make contact a depositing-arc is initiated and the rod material melts off, forming a pool of molten metal on the disc which eventually extends to the wall of the mould. Owing to the high thermal conductivity of the copper and the rapid heat extraction, the molten metal freezes rapidly as it comes into contact with the copper and no melting of the copper takes place. As more molten metal is added to the pool, progressive solidification takes place from the bottom and sides of the melt, so that at any instant only a small crescent-shaped pool of metal is molten. It will be appreciated that thermal factors are of great importance in affecting the as-cast ingot structure.

THERMAL FACTORS AFFECTING THE AS-CAST INGOT STRUCTURE

The heat input to the pool depends on several factors; the arc voltage and current,

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arc length, geometric position of the arc in relation to the mould walls, the partition of the arc's energy at the positive and negative poles, and heat losses. The rate of solidification is primarily dependent on the rate of heat abstraction by the mould and is, therefore, affected by the mould thickness, and the rate of flow and temperature of the cooling water. The overall solidification rate, as would be expected, is related to the ingot size, being rapid for small one-inch diameter ingots and decreasing as the size is increased to about four inches; between four and eight inches diameter there is but little change in the as-cast macro-structure. The effect of mould thickness on the rate of solidification has been studied by depositing molybdenum in a circular water-cooled copper mould in which the wall thickness varied evenly between 1 and 10 mm around the perimeter. It was found that the solidification centre was displaced away from the geometric centre. A similar result was obtained in another experiment; in this the axis of the electrode, and hence of the arc was deliberately displaced from the centre of a constant wall-thickness mould. Again, a similar result is obtained when the arc is deflected to one side by either mechanical or magnetic means.

As true equilibrium never occurs in arc-melted ingots any reference to an as-cast macro-structure should be related to a particular portion of an ingot. It has been found convenient to regard an ingot as consisting of three distinct sections, (a) the non-equilibrium zone at the bottom, (b) the zone of pseudo-equilibrium and, (c) the non-equilibrium zone at the top. A photograph and corresponding schematic drawing of these are shown in Fig. 1. The first non-equilibrium zone starts at the base plug and is, therefore, the first formed portion of the ingot. In it the orientation of the

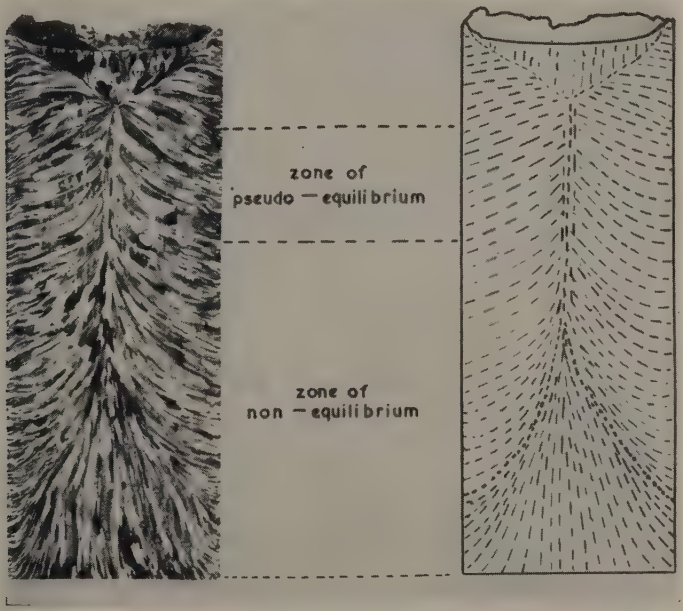

Fig. 1. Zones of pseudo-equilibrium and non-equilibrium in an arc-cast ingot.

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columnar grains varies progressively owing to the higher initial solidification rate which results from the greater heat losses through the water-cooled base. The position at which the change in orientation slows down and becomes constant is fairly well marked and is taken as the start of the zone of pseudo-equilibrium. In this zone, whatever its length, the orientation of the columnar grains does not materially change; the odd instances of appreciable variations encountered in the past have usually been related to incidental variations in the many factors (for instance, arc length) which affect the rate of solidification. The orientation is mainly a function of ingot diameter and burn-off rate. Once the arc is broken, at the termination of melting, the continuity of orientational constancy is broken and this is the start of the upper non-equilibrium zone, the maximum size of which is determined by the depth of molten pool. This zone sometimes consists of small equiaxial crystals which tend to form when the temperature gradients are small and the cooling is multi-directional; columnar grain formation is enhanced by high temperature gradients and uni-directional cooling. The true shape and depth of the molten pool cannot, as is so often assumed, be determined from the as-cast grain structure; usually the pool depth is greater than that estimated from the macro-structure.

As the vertical mould walls are chilled and the hottest portion of the molten pool is at the centre top, the temperature gradients normal to the growing surface are always greater than those parallel to the growing surface; thus, according to NORTHCOTT[4], conditions favourable to columnar growth exist in the melt. The fact that columnar growth is in a direction normal to the solidus contour is of particular significance because the shape of the molten pool and hence the liquid-solid interface can be varied very considerably by changes in the heat input, *i.e.* mainly the burn-off rate. If a mould were filled instantaneously the columnar grains, within the pseudo-equilibrium zone, would lie almost horizontally; in contrast, they would be almost vertical if the mould were filled infinitely slowly and the molten pool were flat. Although such extremes cannot be achieved in practice very large differences in orientation can be produced as shown in Fig. 2.

Simple reasoning shows that the *entire* length of columnar grains, within the pseudo-equilibrium zone cannot be parabolic in shape. By ignoring the central $^1/_2$-inch portion of 2-inch diameter ingots, however, and assuming that growth commences normal to the mould, it has been found that the shapes are, in fact, parabolic with the experi-

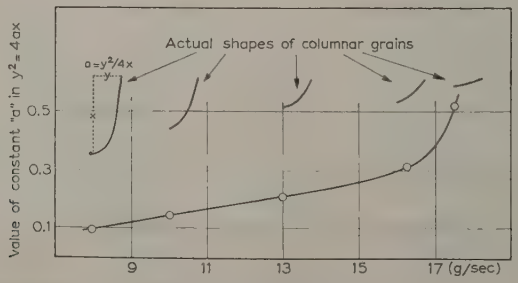

Fig. 2. Relationship between burn-off rate and orientation of columnar grains in a two-inch diameter molybdenum ingot.

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mental scatter. By plotting the constant "a", in the parabolic equation $v^2 = 4ax$, against the burn-off rate the curve in the graph, Fig. 2, was constructed. The actual orientations of the grains corresponding to the points on the curve are also shown. As the research is not yet completed care should be taken in using these results for theoretical studies.

The results, in Fig. 2, imply that the depth of molten pool varies with burn-off rate, this indeed is the case as may be seen from Fig. 3. The depth of molten pool was determined from axial cross-sections of a series of ingots in which the consumable-electrode had been impacted into the molten pool during the melting operation. Corrections were made for displacement. The data are being used in connection with thermodynamic studies and also to relate grain structure with rolling techniques and the mechanical properties obtained therefrom.

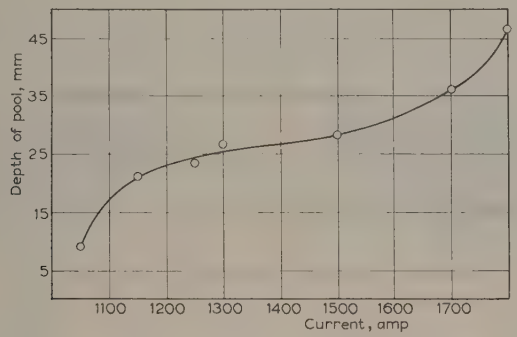

Fig. 3. Effect of arc-current on the depth of molten pool in two-inch diameter molybdenum ingots.

ELECTRO-MAGNETIC STIRRING

Magnetic stirring of the molten pool during melting is a most important mechanical factor affecting the grain structure. This is done by placing a solenoid around the mould. As most of the current flow is at right angles to the electrode and is normal to the magnetic field, motion in the form of stirring must result and the direction of rotation can be found by the application of Fleming's motor rule. The rate of stirring is governed by both the arc current and the strength of magnetic flux. Magnetic stirring minimises alloy segregation and may also refine the structure by creating, seemingly, columnar grains which are shorter than those produced under similar conditions without stirring. An interesting fact is that circumferential sections of spun ingots show that the columnar growth may be non-radial (Fig. 4) to the extent of about 35 degrees. A similar phenomenon, reported by NORTHCOTT[5], has been observed in centrifugal castings produced by conventional methods. The optimum conditions for magnetic stirring are fairly critical and must be determined experimentally. An excessive stirring rate produces thick upstands at the top of the ingot and makes melting difficult. The structure of the upstand is a little finer than normal probably because the solidification rate is higher; this fineness may extend towards the centre of the ingot.

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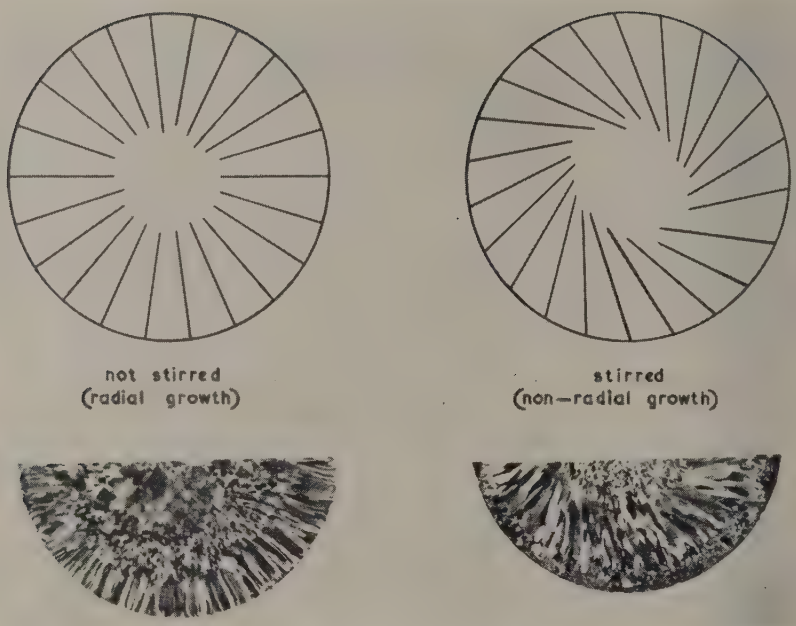

Fig. 4. Magnetic stirring of the molten pool may cause non-radial growth of the columnar grains.

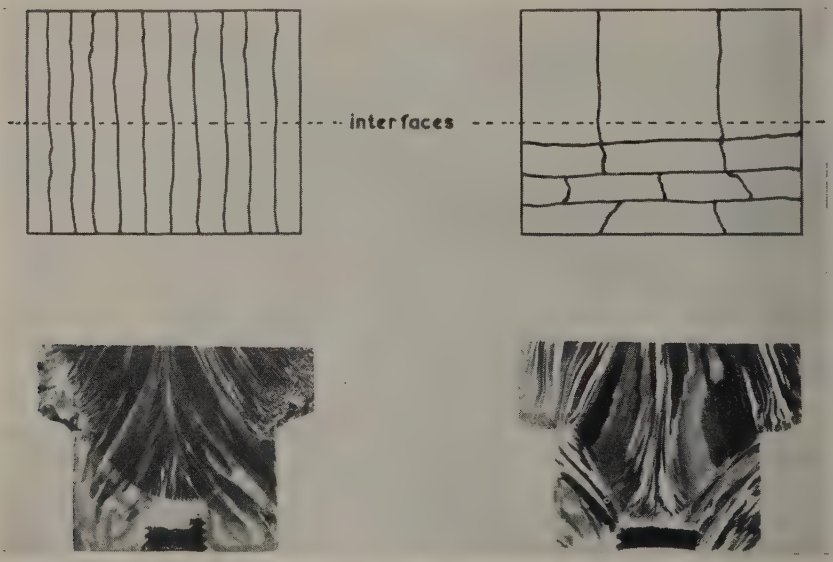

Fig. 5. The orientation of a substrate and a deposit upon it may initially be identical, *i.e.* epitaxical

PHYSICAL FACTORS

Epitaxy is the term used to describe the continuity of crystallographic orientation which occurs across an interface when one metal is deposited upon another; this is illustrated in Fig. 5. Although the deposited metal initially consists of columnar grains possessing the same crystallographic orientation as the substrate, subsequent growth may not be the same owing to preferred orientation effects and the consequent stifling of unfavourably oriented grains. The significance of epitaxy in arc-melted ingots has not yet fully been determined but it is thought that the phenomenon may be turned to practical advantage. For example, a single crystal 2 inches long was produced in the centre of a molybdenum ingot — epitaxical growth having occurred on a $^3/_8$-inch diameter single crystal which had previously been inserted in the base plug.

Columnar grains grown from a metallic melt tend to grow with a particular orientation and the text book example of this is shown in Fig. 6. At the mould wall chill crystallites of random orientation are first deposited, probably as a result of undercooling. Because growth occurs preferentially the favourably oriented grains grow at the expense of the others which are therefore stifled out of a continuing existence.

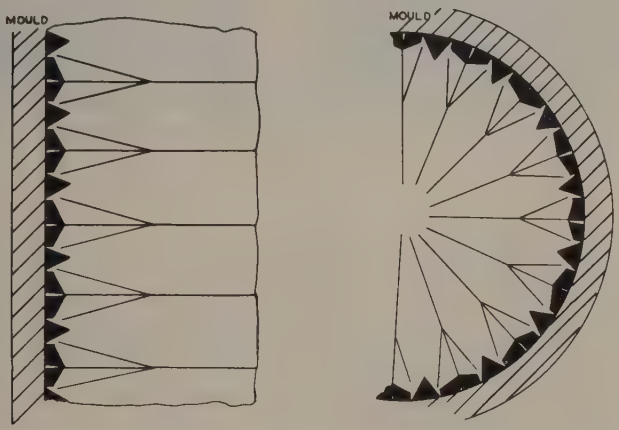

Fig. 6. Growth of unfavourably oriented grains is stifled by the ones with preferred orientations.

INGOTISM

In common with the conventional methods of casting the problem of ingotism, in arc-melted ingots, arises only when the cross-sectional shape of the ingot is unsuitable. The phenomenon is so well known (for example, in square section ingots) that it need not be discussed in this paper. Although circular moulds are usually used in the arc-melting processes there is an indication that other shapes may be used in the future, especially when the ingots are to be rolled down into sheet or plate. In this event, the possibility of ingotism must be considered as this would be more detrimental in the case of the refractory metals than in the commoner metals and alloys.

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UNDERCOOLING

No data are available on the degree of undercooling for the higher-melting-point metals because of experimental difficulties. Observations do, however, indicate that it may occur in molybdenum, for example, chill crystals at the mould walls, and small equiaxed crystals in the top portion of ingots, which, incidentally, possess a low density owing to solidification shrinkage. Dendrites are sometimes seen on the top surface of ingots (Fig. 7); for clarity both a positive and a negative print of the photograph is shown.

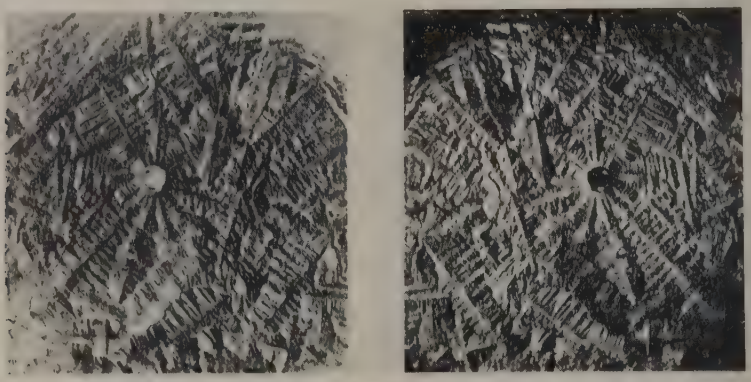

Fig. 7. Dendrites on the surface of a carbon-deoxidised molybdenum ingot.

NUCLEATION

In conventional casting metallurgy the type of solidification — equiaxial, columnar or dendritic — obtained in a given instance is partially determined by the nature and amount of impurities which may be present. When fine as-cast structures are required nucleating agents are often added to the melts. These are substances which, when added to the molten metal provide, or produce by reaction in the melt, highly efficient nuclei capable of initiating crystallite formation with a minimum of undercooling. Nucleants are usually high melting-point substances such as nitrides, borides and carbides. Up to date, unfortunately, no really satisfactory nucleating agent has been discovered for molybdenum.

ALLOYING

Apart from adding nucleants, the addition of certain alloying elements may also change the type and size of grains, whether these are of a columnar, dendritic or equiaxial nature. This depends on the degree of constitutional undercooling[6] produced, which in turn depends upon factors such as the freezing range of the alloy, the rate of solidification and the rate of diffusion in the liquid and solid. A short freezing rate tends to promote columnar solidification. The effects produced by certain elements on the as-cast structure of carbon-deoxidised molybdenum are tabulated and related to three types of macro-structure (see Fig. 8).

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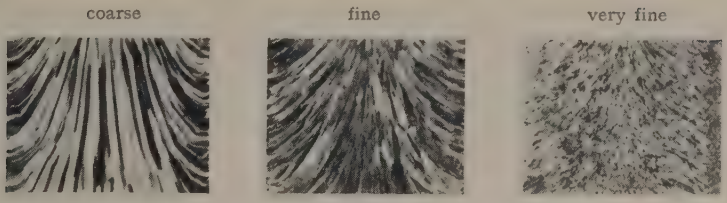

Fig. 8. The effect of alloying elements on the as-cast macro structure of carbon-deoxidised molybdenum.

element	%	%	%
Al	1.0	1.0–3.0	—
Be	0.05	0.05–0.3	—
Co	—	1.0	1.0–2.0
Cr	1.0	1.0–2.5	2.5–4.5
Fe	0.5	—	0.5–2.0
Nb	1.0–4.0	—	—
Ni	0.25	0.25–0.75	0.75–2.5
Si	0.3	0.3–0.4	0.4–0.6
Ti	2.0	2.0–3.0	3.0–2.0
U	0.4	0.4–1.8	—
V	—	1.0–2.0	2.0–9.0
W	—	10.0	—
Zr	—	1.0	1.0–3.0

ACKNOWLEDGEMENT

It is a pleasure to thank Messrs. D. O. PICKMAN and D. T. RICHARDS for their kind assistance during the course of the investigation.

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AN EXAMINATION OF PART OF THE TITANIUM–CARBON SYSTEM*

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INTRODUCTION

Titanium carbon alloys have aroused interest because of the beneficial effect of carbon on the Young's modulus of titanium[1]. As part of a study of alloys of this system we have examined the liquidus at the titanium-rich end of the phase diagram up to 1763°C. Some evidence had previously been obtained that the true liquidus curve might differ considerably from the one published by CADOFF AND NIELSEN[2].

TANTALUM RESISTOR FURNACE

A quenching technique was employed, in a tantalum resistor vacuum furnace which had been developed for use up to about 2100°C. Specimens were heated in closely fitting graphite containers in this furnace at a number of given temperatures for periods up to 8 hours, followed by quenching and analysing.

Specimens were quenched by allowing a hinged door to open and the specimen container to fall into a quenching tank containing vacuum oil which was attached to the outer case. Fig. 1 gives an exterior view of the equipment with the quenching tank in position. A heating element of the split tube type, shown in Fig. 2, was used because of the resulting simplicity of the electrical connections and screen assembly; this construction led incidentally to a high efficiency furnace with low end losses, and it allowed for the thermal expansion of all hot parts.

Tantalum was chosen for the heating element because it was easier to form than tungsten and because it did not become so fragile when heated to high temperatures as either the tungsten or molybdenum sheet available. To prevent distortion at high temperatures a number of semicircular segments were spot welded to the resistor at intervals of about half an inch.

The general arrangement of the interior of the furnace is shown in Fig. 3.

The heating element was 1 inch in diameter, 12 inches long. It was spot welded to tantalum lugs (Q), which were fixed by tungsten grub screws to two 1/4-inch tungsten rods (D).

The brass head (A) incorporated a connection to a vacuum line and a double Wilson seal; through this was introduced the thermocouple (B). The head was joined to the uppermost of two water-cooled brass rings (C) which were insulated from one another. They were connected to the power supply. The two 1/4-inch tungsten rods, (D), screwed into these rings and fitted with short lengths of alumina sleeving (E) where they

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passed through the screen assembly, carried the current to the resistor (F). This was enclosed in a box of radiation screens (H), which was hung from the brass rods (G) by the insulated suspension (I). Molybdenum sheet was used for the screens. The vertical ones were formed from a tight sheet spiral, and the horizontal ones were discs lying one upon another, kept apart by centre-punch indentations. There was a tubular

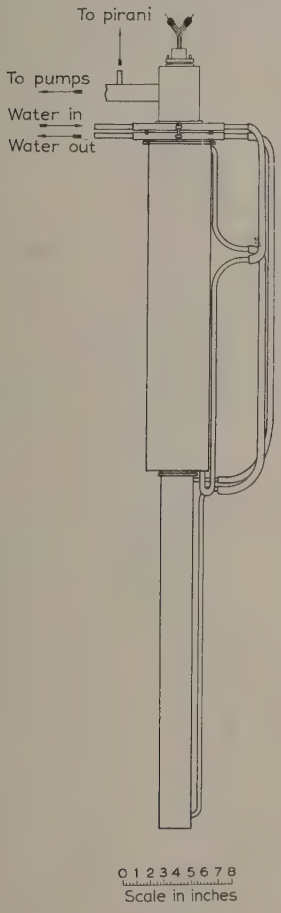

Fig. 1. Exterior view of the furnace.

Fig. 2. The heating element.

molybdenum liner (R) which fitted into the hole in the bottom horizontal screens. This liner was insulated from the resistor by refractory sleeves (S) near each end. It carried a set of inner horizontal screens at the top of the furnace, similarly insulated, and its main function was to safeguard the resistor from contact with material from the specimen.

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The specimen container (W) was supported by a length of thin walled molybdenum channelling (V) attached to a heavy molybdenum component (U) filled with discs. The whole of this assembly fell into the quenching tank (P) on opening the trap door (T) by fusing the wire (L). This method worked satisfactorily at temperatures up to about 1800 C. The components (K), (M), (H) and (J) provided electrical connection to the wire (L). The clamp (M) also held the alumina thermocouple sheath (N). The tip of the sheath was separated from the specimen container by a molybdenum disc.

Since the efficiency of molybdenum radiation screens varies with furnace conditions

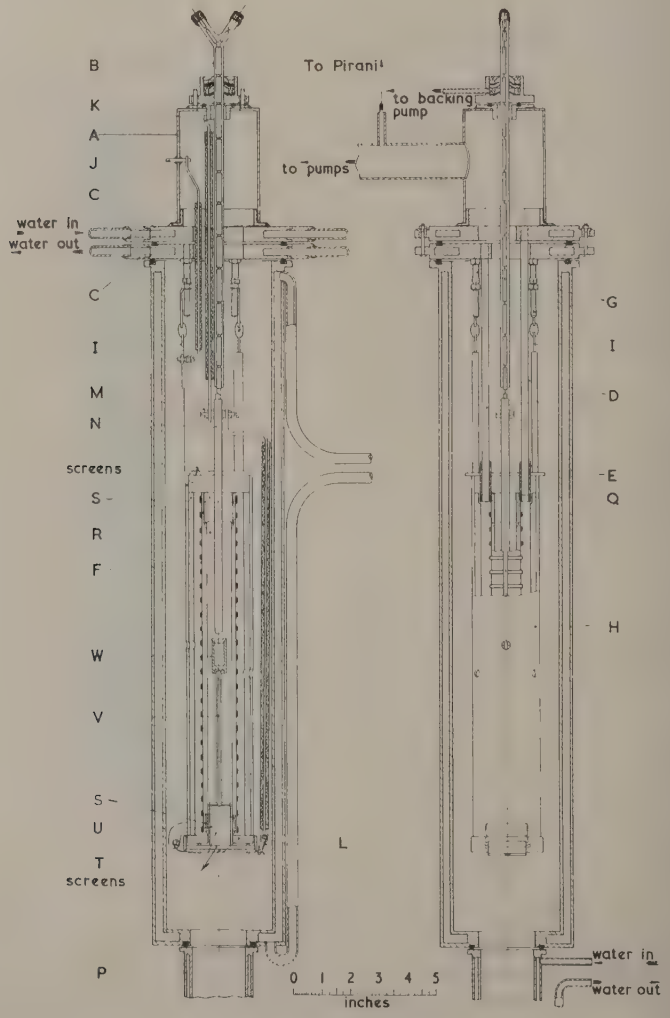

Fig. 3. Details of tantalum furnace.

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and the screens frequently deteriorate rapidly, especially when run at intermediate temperatures, due to the deposition of material evaporated from the hotter parts of the furnace, it was decided to have so many surfaces that under all running conditions the outermost screens would be below red heat. Under these conditions the main heat loss would be due to radiation through small fixed gaps in the screening and to conduction along the tungsten leads and the thermocouple insulation; the performance of the furnace, and in particular the temperature distribution, would therefore be relatively insensitive to changes in the efficiency of individual screens.

About eighteen screens were needed to produce the desired effect, and in this state the furnace required about 850 watts to reach 1730°C. There was however a temperature peak near the centre because of the heat loss at the ends, and in order to counterbalance this, several small holes were made in the screens near the hottest part. The first empirical correction of this sort resulted in a 4-cm length with a variation of $\pm$ 1.6°C over the full temperature range, and this was considered adequate for the present purpose. The furnace was run off a low voltage a.c. supply, and took 120 A at 9.3 V at 1768°C.

The system was evacuated by an oil diffusion pump. A high speed vacuum line was not necessary because there were hardly any refractory components present, and therefore no large source of occluded gas.

The apparatus could be run for short periods up to 2100°C provided thoria was used in place of alumina for the refractory parts. It was run for prolonged periods up to 1800°C with alumina parts.

TUNGSTEN–IRIDIUM THERMOCOUPLE

For the titanium–carbon investigation a tungsten–iridium thermocouple was used. TROY AND STEVEN[3] had shown that good results could be obtained with this couple; it produced a higher e.m.f. than the platinum–platinum/13% rhodium and tungsten–molybdenum couples; there was no inversion, and the thermoelectric power was almost constant above 1000°C; no change in the output of the couple could be detected during heating for 120 hours at 1900 to 2000°C. We confirmed the results of TROY AND STEVEN, and for the present purpose the couple was calibrated against a standard platinum–platinum/13% rhodium couple and checked at the melting points of palladium and platinum. Repeated measurements at the palladium point showed that the performance of the couple was not changing during the course of the experiments. The e.m.f.–temperature curve is shown in Fig. 4; it has a slope of 0.026 mV per degree. To make the hot junction the two wires were bound together with fine tungsten wire about half an inch from the end of the iridium wire. The iridium was then melted back in a carbon arc and formed a bead round the tungsten.

DETERMINATION OF PART OF THE TITANIUM–CARBON LIQUIDUS CURVE

The difficulties associated with the determination of the liquidus curves of titanium systems are well known. The problem has been discussed by HUME-ROTHERY AND POOLE[4]. To limit contamination from the container, one can either work with short heating periods or choose as container an alloy which is close to the solidus composition for the temperature concerned. The latter approach was adopted here; however although a few experiments were done with titanium carbide crucibles, it was found

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more convenient to use pure graphite crucibles and to allow the solid carbide phase to form on the crucible wall during the course of the experiment.

Crucibles with closely fitting lids were made from a specially purified high density graphite supplied by the Morgan Crucible Co. in which spectrographic analysis indicated only traces of boron and silicon. Titanium specimens 3/8 inch diameter by 7/8 inch long were machined to fit inside these. They were heated in vacuo at various temperatures, quenched, examined metallographically and chemically analysed.

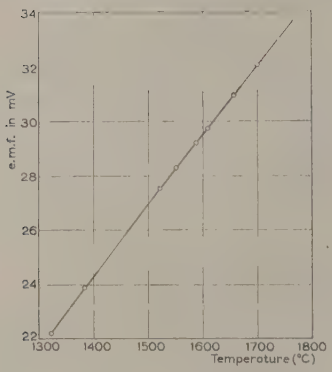

Fig. 4. E.m.f. *vs.* temperature for tungsten–iridium thermocouple.

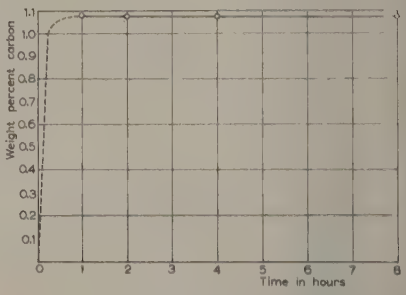

Fig. 5. Carbon content *vs.* heating period.

A layer of titanium carbide formed at the solid–liquid interface and increased slowly in thickness. In experiments at 1680°C* it was found that after 1 hour the carbide layer was 0.009 cm thick and after 2 hours it was 0.012 cm thick. The melt took up carbon from the crucible rapidly at first; but after the initial period of relatively rapid change, further alteration in melt composition at a given temperature became extremely slow. This is illustrated in Fig. 5 which shows the carbon content of the melt after heating periods between 1 and 8 hours at 1650°C (using arc melted magnesium reduced titanium). After the first hour no further change in melt composition could be detected.

As we now had a system in which the solid TiC phase was growing into the melt at a very slow rate, and the composition of the melt was changing extremely slowly, it was considered that after 1 hour's heating the melt composition was near enough to its final value for the present purpose, and that this technique could be used to give a point on the liquidus curve, though of course the system as a whole was not at equilibrium.

Using Van Arkel titanium from the Foote Mineral Co. with a Vickers hardness of 80, the principle impurity being zirconium, the results shown in Table 1 were obtained.

The melting point of the titanium used was found to be 1667 ± 8°C. These results therefore suggested a eutectic system with a eutectic between 1644 and 1650°C.

In order to determine the eutectic temperature more precisely, small pieces of Van Arkel titanium were heated in graphite crucibles to temperatures between 1640 and

* Except where otherwise stated temperatures are accurate to ± 7°C.

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TABLE I

Temp. °C	*Carbon content of melt (at.-%)*
1644	(specimen did not melt)
1650	4.51
1668	4.84
1688	5.10
1763	6.31

646°C. Melting occurred at 1646 but not at 1644°C and the eutectic is therefore onsidered to be at 1645 ± 8°C.

Specimens quenched from near the eutectic temperature had a fine carbide distri-ution; after quenching from a higher temperature (1688°C) carbide dendrites were ound.

These observations differed markedly from those of CADOFF AND NIELSEN, whose esults are shown in Fig. 6. Attempts were made therefore to confirm the existence f a eutectic by a method previously used for determination of the titanium melting oint. In the melting-point experiments a graphite pot with a well fitting lid had been oated on the inside with a layer of titanium carbide by evaporation of titanium on o the inner surface. The crucible is shown in Fig. 7. A fine tungsten wire ending in loop passed through a hole in the lid, and from it the specimen could be suspended. eing surrounded by a titanium carbide box inside the graphite the specimen was rotected from contamination. It was taken up to a given temperature in vacuo in ie tantalum furnace, held there for 10 minutes and cooled in situ. Fig. 8 gives some esults with a sample of Van Arkel titanium heated to temperatures between 1670 nd 1678°C. Several titanium specimens were treated in this way and results were otained which agreed well with other published figures for the melting point (*i.e.* elting points of 1667 to 1671 ± 8°C.) No evidence for gross contamination was found.

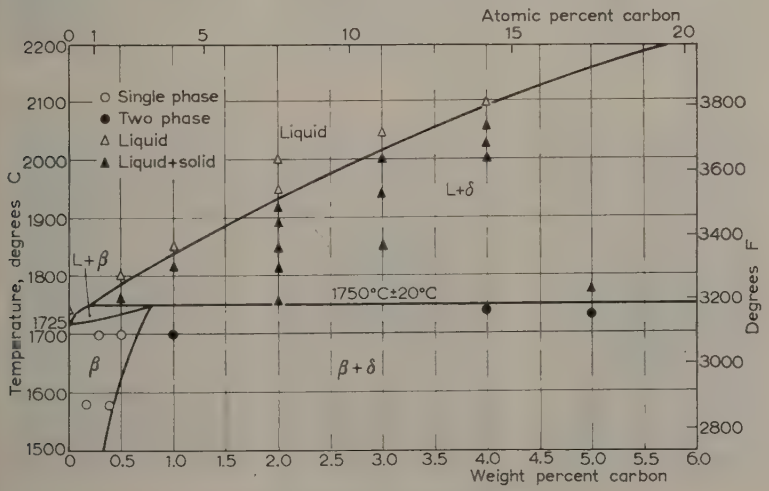

Fig. 6. Results of CADOFF AND NIELSEN.

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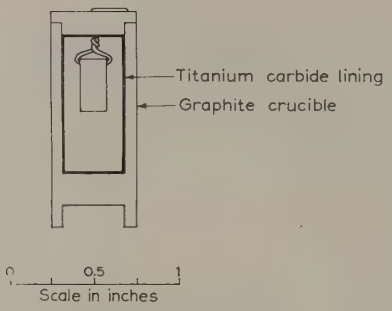

Fig. 7. The crucible.

This technique was used therefore with a titanium–carbon alloy specimen containing 4.39 at.-% carbon made from Van Arkel titanium by arc melting, and it was found

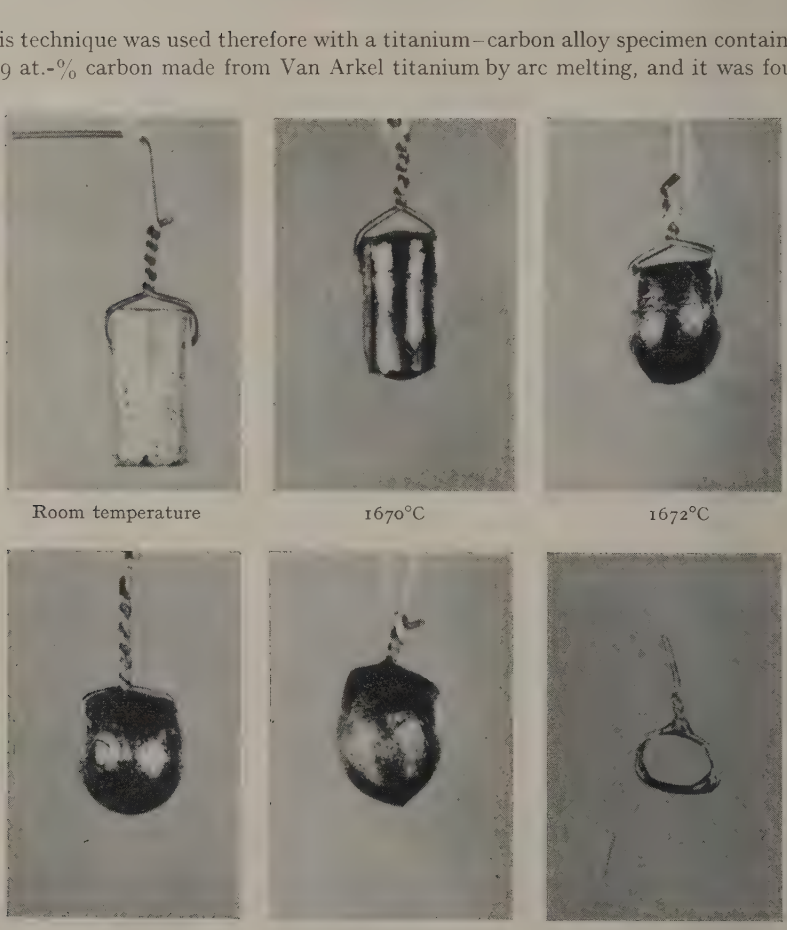

Fig. 8. Results with Van Arkel titanium heated to 1670–1678°C.

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hat after 10 minutes at 1650°C the specimen had melted into a bead. This suggested hat the depression in the freezing point was not due to an unidentified impurity.

SOLIDUS EXPERIMENTS

A few experiments were made on the solidus. Alloys were made from Van Arkel itanium and titanium carbide by arc melting twice, forging to 1/4-inch bar, removing he contaminated surface region and vacuum annealing. Specimens were wrapped n tungsten foil, placed in a titanium container, and heated for 2 hours at various emperatures in the tantalum furnace followed by quenching.

TABLE II

Heat treatment temp. °C	*Carbon content (at.-%)* *a) No carbide*	*b) Carbide*
1558	0.52	0.59
1602	—	0.59
1639	0.52	0.59
1652	0.20	0.40
1660	—	0.20

The carbon contents are accurate to ± 0.08%.

CONCLUSION

The above results, together with those on the liquids are given in Fig. 9. The eutectic vas found to be at 4.39 at.-% C and 1645 ± 8°C. The solubility of carbon in β-titanium t the eutectic temperature and at 1558°C was 0.55 at.-%.

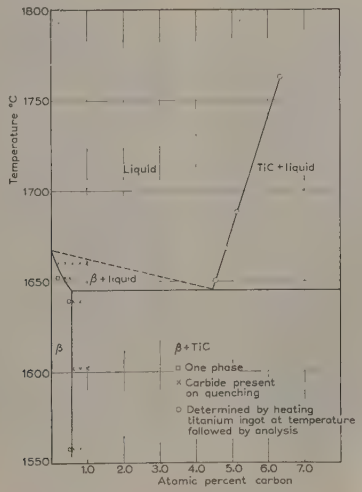

Fig. 9. Part of phase diagram.

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ZONE REFINING OF MOLYBDENUM

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FURNACE REQUIREMENTS

The electron bombardment floating zone melting method[1] has been applied to refining molybdenum. A mercury diffusion pump provides the vacuum and the furnace design, electrical supply and control equipment is based on that used at S.E.R.L.[2]. Only slight mechanical modifications to the furnace are necessary to melt 3/8 and 1/2-inch diameter molybdenum rod. Upward zone movement was adopted as standard as this gives a more stable liquid zone.

The power P required to melt a rod of diameter d is found to follow a formula of the type

$$P = Ad + Bd^2$$

The constant A is proportional to the fourth power of the absolute melting point while B is proportional to the thermal conductivity near the melting point. This formula although only approximate enables the electrical equipment to be set up or

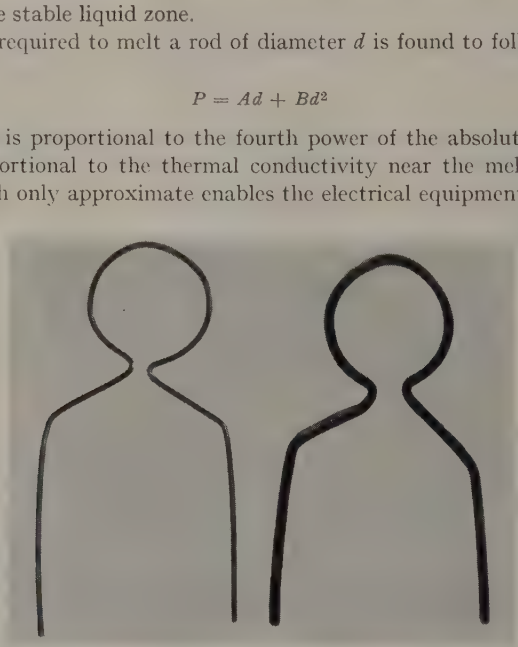

Fig. 1. Wire filament before and after rolling.

its correct range when a new diameter or material is to be zoned. For molybdenum the power required to melt 1/8 and 1/2-inch diameter rods is 260 watts and 2140 watts respectively.

During the zoning of a 1/4-inch diameter molybdenum rod 13% is lost due to eva

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poration from the liquid zone. Much of this metal is deposited on the filament. Not only does this increase the weight of the filament and so cause it to sag, but it reduces its resistance and so the current required to keep it at temperature increases. To overcome these difficulties 28 thou. tungsten wire filaments were made up heated to red heat and rolled to 11 thou. in thickness. A wire filament and a rolled filament are shown in Fig. 1. It will be seen that the area of filament exposed to the liquid zone is much smaller. This design has increased filament life from about half an hour to an hour.

GROWTH OF LIQUID ZONE

The growth of the liquid zone with power input was studied for 1/4-inch molybdenum rod. Fig. 2 shows the shape of the zone when the surface of the rod just melts, and Figs. 3-6 show how it increases. The power required to melt right through the rod is only 10% more than that required to melt the surface.

Fig. 2. Section of 1/4-inch rod. Molten zone at 682 watts.

Fig. 3. Section of 1/4-inch rod. Molten zone at 710 watts.

ORIENTATION OF CRYSTALS

If the rod is molten through the resulting zone refined bar is a single crystal. It is necessary to know the orientation of the crystals for deformation studies but also

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interesting to know whether there is any preferred orientation. The crystals were oriented by X-ray back reflection and Fig. 7 shows the unit stereographic triangle with the axes of the zone refined crystals marked. There is no preferred orientation within the region (001) (101) (112), but it is noteworthy that none of the axes come outside this region. There is also no trend of orientation with purity at least over the range 0.01 to 0.001 wt.-% carbon.

Fig. 4. Section of 1/4-inch rod. Molten zone at 736 watts.

Fig. 5. Section of 1/4-inch rod. Molten zone at 760 watts.

ANALYSIS

The analysis of a few parts per million of carbon in a 2 g sample of molybdenum is very difficult. An apparatus has been developed in the Armament Research and Development Establishment which has a sensitivity of 7 p.p.m. on a 2 g sample, and it is analyses of this type which are reported here. Fig. 8 shows the variation of carbon content along a 3/8-inch diameter rod zoned twice at 3 mm/min. The shape of the carbon distribution is about what was expected. However Fig. 9 shows the same plot for another exactly similar rod. The two high values at the supposed pure end of the rod may be due to the fact that the rod was not a single crystal for the first cm of its

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ength and the carbon may have diffused back along the grain boundaries during zoning. This point will be investigated in the near future. The analysis results as a whole indicate that there is some movement of carbon by zone refining but not as much as would be expected from the mechanical tests performed. The carbon is reduced by a factor of four over the majority of the rod and by a factor of ten at the pure end. The number of zone passes does not affect the overall purity of the rods greatly.

MECHANICAL PROPERTIES

The ductility of the zone refined crystals is such that they can be rolled at room temperature to a reduction of some 30% without cracking. Some of the zone refined rods have been tested in tension and impact. The tensile tests were done at room temperature in three places on rods which had varying carbon contents along their

Fig. 6. Section of 1/4-inch rod. Molten zone at 773 watts.

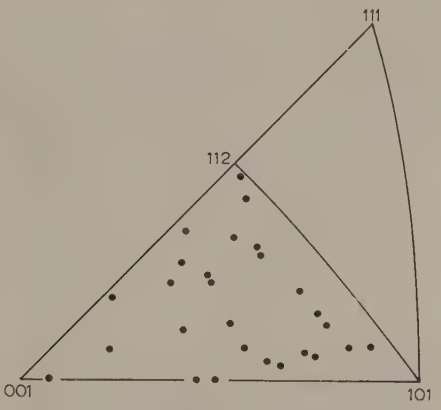

Fig. 7. Unit stereographic triangle showing axes of zone refined crystals marked.

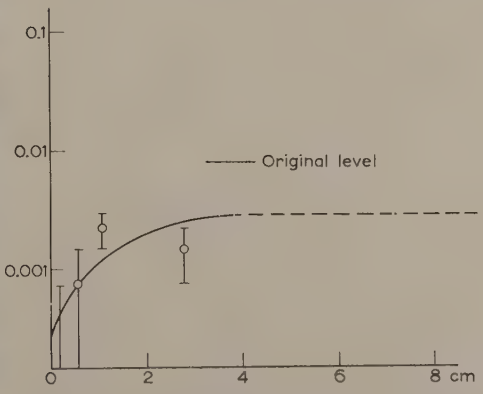

Fig. 8. Carbon content *vs.* distance for 3/8-inch molybdenum rod.

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length. Fig. 10 shows the curves for the purest and least pure ends of one such crystal. The sharp yield point is not apparent in the pure condition and the breaking load is too small to measure. The carbon content in this case is about 0.001 wt.-%. The yield point returns at about 0.004 wt.-%.

The impact tests were done on un-notched as grown 1/4-inch diameter crystals in a 10 ft.lb. Charpy machine. The temperature *vs.* energy absorbed graphs are shown in Fig. 11. The 5 ft.lb. transition temperatures vary with carbon content as follows:

0.001% carbon : —180°C
0.002% carbon : —140°C
0.008% carbon : —40°C

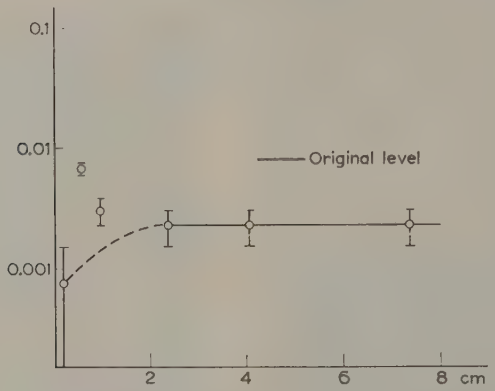

Fig. 9. Carbon content *vs.* distance for 3/8-inch molybdenum rod.

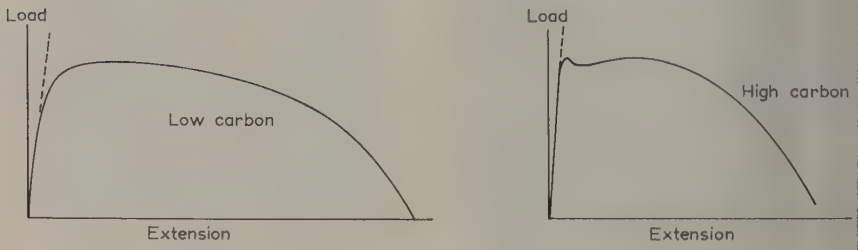

Fig. 10. Stress-strain curves for both ends of a zone refined crystal.

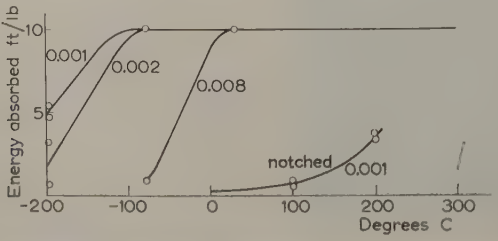

Fig. 11. Energy absorbed *vs.* temperature for various purity molybdenum single crystals.

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When a notch was ground into the 0.001% carbon crystals the transition temperature rose to 230°C. This represents the worst condition since the specimen was not annealed after notching nor was the notch polished. However even this is encouraging since the lowest impact transition temperature for normal notched polycrystalline molybdenum is 350°C. It follows that molybdenum is inherently a very ductile metal even at low temperatures and that carbon in solution in molybdenum causes extreme strain rate sensitivity. It is also clear that molybdenum is strongly notch sensitive or surface sensitive even in pure single crystal form. The properties of pure polycrystalline zone refined molybdenum will be tested very soon.

ACKNOWLEDGEMENT

My thanks are due to my colleagues C. A. WHITTINGHAM, who designed and built much of the apparatus, and G. H. COCKETT who provided the X-ray data.

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THE ZONE MELTING OF REFRACTORY METALS INCLUDING RHENIUM AND TUNGSTEN

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INTRODUCTION

Zone melting is an attractive method for the purification of certain metals and also for growing single crystals. It is particularly valuable for preparing large crystals of the refractory metals which are difficult to handle by other crystal growing methods.

With refractory and reactive metals it is necessary to avoid conventional crucible materials. Two techniques make this possible; in one, arc melting on a water cooled copper hearth is used[1-4] and in the other electron bombardment melting of a "floating zone" in a vertical bar[5]. We have found arc melting techniques to be the more useful for zone refining although the zone melted bars are usually polycrystalline. The electron bombardment technique produces single crystals; the metal is frequently purified during the process, mainly by vacuum melting but in some cases also by zone refining. The use of the latter technique for zone refining is usually limited to those cases in which zone speeds greater than about 1 mm/min are suitable as most metals have a rather high vapour pressure ($> 10^{-3}$ mm) at their melting point and evaporation losses are considerable at lower speeds with some metals.

THE ARC ZONE MELTING FURNACE

The arc zone melting furnace is basically an argon arc furnace in which the arc is used to melt a short length of a specimen which is moved horizontally under the arc. A diagram of the furnace is shown in Fig. 1. The tungsten electrode can move vertically and be fixed in any desired position. The hearth consists of a water cooled copper tube with a V-shaped groove pressed into it to support the specimen. The hearth can be drawn along steadily at speeds in the range 0.0015–0.5 inch/min, by means of the concentric inlet and outlet water tubes which pass through a Wilson seal; the inlet water tube is fixed relative to the tungsten electrode so that the water is always introduced directly under the arc.

Zone melting is carried out in purified argon at a pressure of $\sim 1/3$–1 atm, the last traces of impurity being removed from the atmosphere before zone melting by gettering with a molten titanium bead for about 5–10 min. The hearth is then moved manually so that the specimen is under the arc which is then adjusted to give a suitably sized zone and the hearth is set to move at the desired speed.

During a zone pass the arc has a tendency to "wander" which is undesirable. This can be overcome by applying a magnetic field to the arc. A field of about 2000 gauss which can be obtained from a pair of permanent magnets is ample. The wandering

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can be decreased by increasing the argon pressure or by reducing the electrode–specimen distance to about $^1/_{16}$–$^1/_8$ inch.

Some difficulty is experienced with the present design from contamination of the specimen by the products of outgassing of the hearth. These are not evolved until the hearth is heated so that they are evolved in intimate contact with the hot specimen.

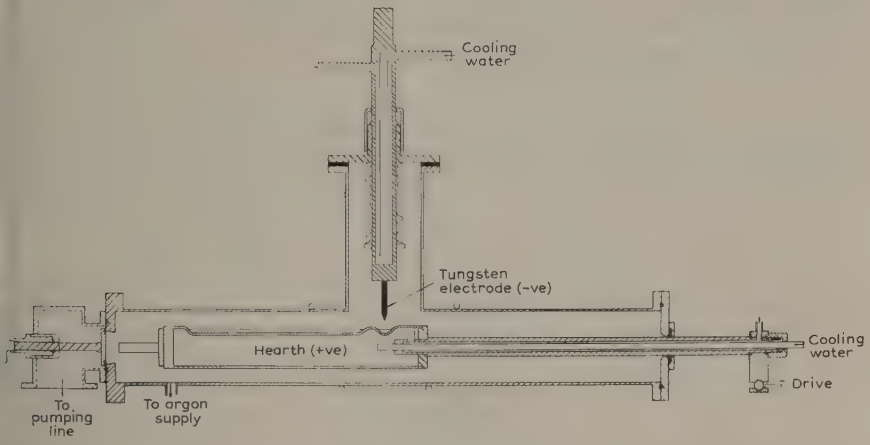

Fig. 1. Arc zone melting furnace.

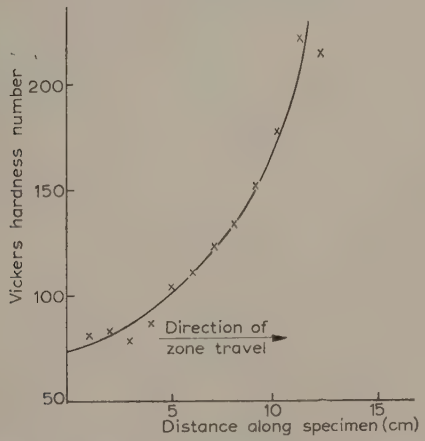

Fig. 2. Hardness of vanadium after zone refining.

It would be desirable in a future furnace to arrange for the hearth to be outgassed before the specimen is loaded.

Although outgassing may be a difficulty in some cases this is not necessarily the case as can be shown by the fact that we have produced considerable zone refining of vanadium as measured by the hardness of the metal (Fig. 2). Starting with some sponge vanadium as supplied by Magnesium Elektron Limited, which has a hard-

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ness of ca. 170–180 V.H.N. after melting in the arc furnace we produced an appreciable quantity of vanadium with a hardness of ca. 80 V.H.N.

Once set up this apparatus is extremely stable so that little attention is required during a zone pass. As the zone moves from the ends to the centre of the specimen the zone size alters as an appreciable amount of heat is removed from the zone by conduction along the bar. The zone size could be adjusted during the pass but it is more desirable to leave it as any adjustment would change the rate of movement of the liquid–solid interface abruptly.

ELECTRON BOMBARDMENT FLOATING ZONE FURNACE

In the floating zone furnace (Fig. 3) electron bombardment heating is used to melt a short length of a vertical specimen in a vacuum of about 10^{-4} to 10^{-5} mm; the liquid being held in position by surface tension. The heater consists of a single turn ($\sim 3/4$ inch

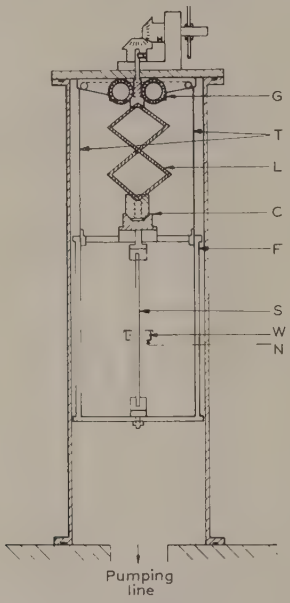

Fig. 3. Electron bombardment floating zone refiner.

dia.) of 0.020 inch dia. tungsten wire which is held at a negative potential of up to —4 kV relative to the specimen. The filament is surrounded by a shield of molybdenum sheet at the same potential as the filament to give some focusing. The specimen is supported at either end in a rigid water cooled frame which can be moved at speeds in the range 0.010 to 0.5 inch/min relative to the heater.

A smoothed full wave rectified power supply capable of supplying up to 1 A emission current at up to 4 kV is used. The emission current is stabilized.

Three features of this apparatus are of major importance:

(1) The pumping system should have sufficient speed to cope with any gas evolved. When melting a zone of $\sim 1/4$ inch dia. in a chamber of about 10 litre an M-V.03B

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iffusion pump backed by a D.R.1 rotary pump giving a pumping speed ∿20–30 l/sec s adequate for most purposes.

(2) The emission current in the furnace may vary rapidly if the specimen outgasses apidly on melting. As a result it is necessary to stabilize the power supply. An account f a suitable stabilizer is given by ALLENDEN[6].

(3) If very small diameter specimens or high melting point metals are to be zone nelted it is important that the ratio filament diameter : specimen diameter be kept s low as possible (less than about 3.1 has been found suitable using 4 kV) or space harge will limit the amount of power that can be put into the specimen. This effect vill be less noticeable at higher potentials.

The starting material used is in the form of as-received metal rods, arc cast ingots r hydrostatically pressed powder. These are usually mounted in two pieces which re welded together before zone melting commences, thus avoiding the difficulty of ligning the ends of the specimen accurately.

When the metal to be treated contains much gas we find the powder specimens to e most suitable. This is especially so in the case of molybdenum and tungsten. On nelting as-received rod gas is evolved in bursts and this, besides raising the pressure ocally, bubbles out of the metal so violently as to distort it, upsetting the electric ield and unless very thin layers of the surface of a specimen are melted in many uccessive passes so as to reduce the rate of gas evolution the emission current is ncontrollable. Starting with a powder specimen it is possible to remove the gas from he metal gradually whilst it is still porous. This occupies less time than previously rc melting the metal or melting the as-received specimen gradually. Specimen sizes re up to 0.3–0.4 inch dia. × 8 inches long of which about a 4 inches length is treated. f a greater length is treated the specimen grips may become overheated.

Many metals have been zone melted in this apparatus (tungsten, rhenium, molybdenum, tantalum, niobium, etc.). The zone melted length of the specimen is a single rystal unless the material has a phase change. We have also produced homogeneous ingle crystals of molybdenum–rhenium alloy containing 35 atomic per cent rhenium. In o case which we have examined has there been any evidence of a preferred orientation.

The single crystals grown by this means appear to be of reasonable quality. In ungsten of which we have most experience, there is a substructure consisting of small grains with a misorientation of about 1° principally rotation about the axis of the specimen. The size of the subgrains is variable and although other variables affect t, the size of the subgrains increases with the speed of the zone pass from approximately 10^{-2} to 10^{-1} cm they are sometimes equiaxed but frequently elongated along he length of the specimen. We believe that this substructure occurs in most of the ingle crystals we have produced.

ACKNOWLEDGEMENT

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ARC-MELTING PROCESSES FOR THE REFRACTORY METALS

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INTRODUCTION

Metals such as molybdenum[1], tantalum and tungsten are particularly susceptible to embrittlement by impurities. The production of solid masses of any of these metals in a high state of purity is not possible at present by a conventional melting and casting process, the fundamental difficulty being the lack of a suitable high-temperature refractory material[2]. This difficulty has been circumvented, however, by the discovery that even the most reactive and refractory metals could be arc-melted and cast in water-cooled copper moulds, in vacuum or inert-gas atmospheres[3]. There is no pick-up of copper and it is further possible, by multiple remelting, to reduce the content of gaseous and volatile impurities to a very low level. The arc-melting processes dealt with in this paper are suitable not only for the refractory metals but also for such high-melting-point metals as titanium and heat-resisting alloys.

THE ELECTRIC ARC

Although the electric arc has been the subject of many researches no single explanation of its fundamental mechanism is universally accepted. For the present purpose, however, the following superficial explanation is adequate. The arc consists of three basic parts, the anode, the cathode and the positive column or plasma. In the cooler zone surrounding the positive column, recombination of atoms may take place with the release of heat; this zone is known as the aureole. The cathode is heated by bombardment of its surface with positive ions and the anode by electrons. The stability of the cathode spot, and hence of the entire arc, is greatly influenced by the chemical and physical conditions of the electrode[4]; by comparison, the importance of the anode is relatively insignificant.

In arc-melting technology two types of arc are recognised, the non-consumable-electrode arc, and the metal-depositing or consumable-electrode arc. Although the fundamental mechanism of the two types of arcs are thought to be similar there are very important practical differences.

The term "non-consumable electrode" is applied to electrodes which do not melt away during arcing; there may be a small loss due to vaporisation but this is not of general significance. They usually consist of graphite or tungsten tips attached to water-cooled conductors, and are connected to the negative pole of a d.c. source, but to be pedantic may consist of any conducting material so long as it is not melted and transferred across the arc. There is a critical operational range of ambient gas pressure for the non-consumable-electrode arc[5] and this varies between about 5 and 40 mm Hg depending on the materials concerned and on the value of the energy input. Below

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his range the arc changes over to a glow-type discharge and is then useless for melting purposes; the arc may be used at any higher pressure.

For the metal-depositing arc[6] (Fig. 1) the consumable electrode may consist of any metal capable of being melted and transferred through the arc. Because of the metal vapour from the superheated molten globules which permeates the entire arc, this type of arc may be used in high-vacuum, or indeed at any pressure. The burn-off

Fig. 1. The metal-depositing arc.

rate of the electrode is roughly proportional to the current used. The globule size may affect ingot quality and is related to the type of current supply; an a.c. supply produces very small globules whereas a d.c. positive polarity electrode produces large globules. The metal-depositing arc may be initiated by contact arcing or by means of a superimposed high-frequency source. The non-consumable-electrode arc is best initiated by high-frequency because with contact arcing there is a danger of contamination due to pick-up. A detailed investigation of the arc characteristics and related electrical aspects has been reported by Moss[4].

BASIC TYPES OF ARC-MELTING FURNACES

There are two basic types of cold-mould arc-melting furnaces, those using non-consumable electrodes and those using consumable ones. In the former a water-cooled electrode tipped with graphite or tungsten is normally used. The raw material is fed into a water-cooled copper mould by an auxiliary feeding device and is melted by the arc. This charge material, especially when consisting of mixtures, should be of uniform size to prevent alloy segregation. In singly melted ingots the rate of feeding should be even and slow enough to ensure complete fusion of the raw material; the

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inclusion of unfused pieces in the ingot may affect its properties. The molten pool should extend to the wall of the mould otherwise excessive machining will be necessary to remove the poor ingot surface. When using a remelting technique it is not always necessary to take such care with the first melted ingot. In order to maintain a constant arc length, as the ingot increases in length, either the electrode must be raised or the ingot must be withdrawn from the bottom of the mould. Although both methods are commonly used the latter method is the preferred one as better visibility of the molten pool and more effective removal of gases is achieved.

In the consumable-electrode arc-melting furnace a preformed electrode of the basic ingot composition is used. The ingot is formed by direct transfer of the fused electrode, in superheated globular form, to the molten pool. Owing to the high thermal conductivity of the copper and the rapid heat extraction, the molten metal freezes rapidly as it comes into contact with the water-cooled copper mould and no melting of the copper takes place. As more metal is added to the pool, progressive solidification takes place from the bottom and sides of the ingot, so that at any instant only a small crescent-shaped pool of metal is molten[2]. The shape and depth of molten pool may be controlled by varying the arc current and arc length. Alloy ingots may be produced by two methods, (a) by using a consumable electrode appropriate to the desired ingot composition, or (b) by using a consumable electrode of the basic ingot composition in conjunction with a separate alloy feeding mechanism. Although the first method is satisfactory, provided that suitable electrodes may be fabricated, it is generally only used when large numbers of ingots are to be made. For experimental melts, where the required ingot composition changes from day to day, it is not economic; for this reason it is better to hold stocks of a single basic material and add the alloying ingredients separately. This may introduce feeding difficulties since there is an optimum size for the alloy additions; small particles tend to be blasted away from the molten pool area by gas streams whilst large particles may not be completely fused. Furthermore, the rate of alloy feed must be related to the burn-off rate from the electrode. Alloy homogeneity is enhanced by using a deep molten pool and may still further be improved by using remelting techniques or by magnetic stirring[7].

CHOICE OF AN ARC-MELTING PROCESS

There is no fixed single rule governing the choice of a particular process. With the consumable-electrode process metal from the electrode is transferred to the pool in a liquid and uncontaminated state. It is a fast process with a high thermal efficiency. Because melting may be carried out in high vacuum the residual gas content is very low and there is some reduction of low-melting point impurities by vaporisation. If ingots containing low-melting-point alloys are desired, melting may be done in an atmosphere of purified inert gas. With the non-consumable-electrode process pick-up of contaminants may be a problem, melting cannot be done in high-vacuum, there is a danger of unfused raw material being occluded in the ingot (this may be eliminated by subsequent remelting), and the thermal efficiency is low. In spite of these disadvantages the process has been used on a large scale for the production of titanium ingots especially in the early days of arc-melting, and before the detrimental effects of hydrogen were realised. The modern trend is certainly towards consumable-electrode processes especially for very large diameter ingots; in this case the electrodes are usually as large in diameter as possible.

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TYPICAL ARC-MELTING FURNACES

As it is not practicable to discuss all furnace designs and modifications only four typical arc-melting units are described.

Fig. 2 shows a dual-purpose arc-melting furnace designed for the production of

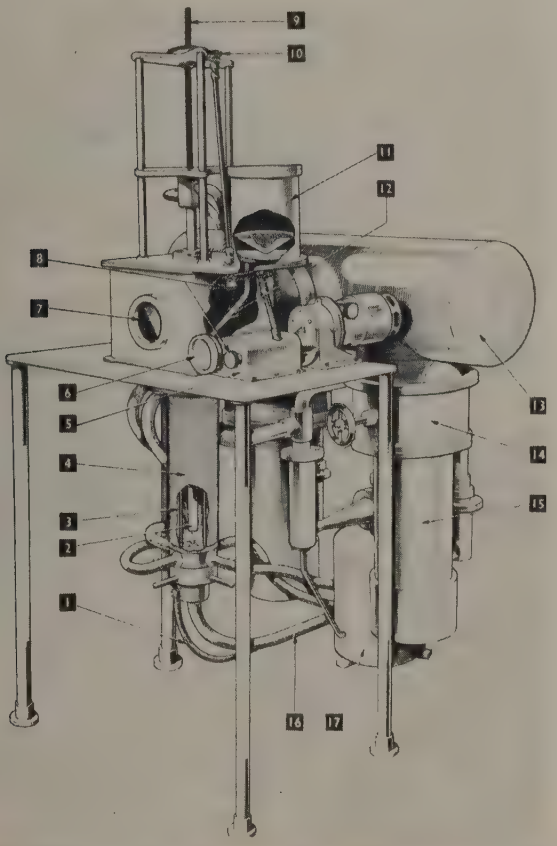

Fig. 2. A non-consumable-electrode arc-melting furnace*.

1. High current cable (d.c. positive)
2. Water-cooled non-consumable electrode
3. Water-cooled copper mould
4. D.c. solenoid
5. Mechanism for synchronising pellet and electrode feed rates
6. Pellet rate meter
7. Inspection window
8. Control knobs
9. Leadscrew and d.c. negative supply
10. Electrode feed
11. Raw material pellet hopper
12. Pellet feed tube to mould
13. High vacuum manifold
14. Baffle valve
15. Diffusion pump
16. Cooling water outlet pipe
17. Booster pump

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ingots between $2^1/_2$ inches and 5 inches diameter. Up to the time of writing, however, it has not yet been put into operation. As illustrated it is set up for use with a non-consumable electrode. The raw material is mixed with the necessary alloying constituents and pressed into spherical compacts. These are stored in a hopper and fed at

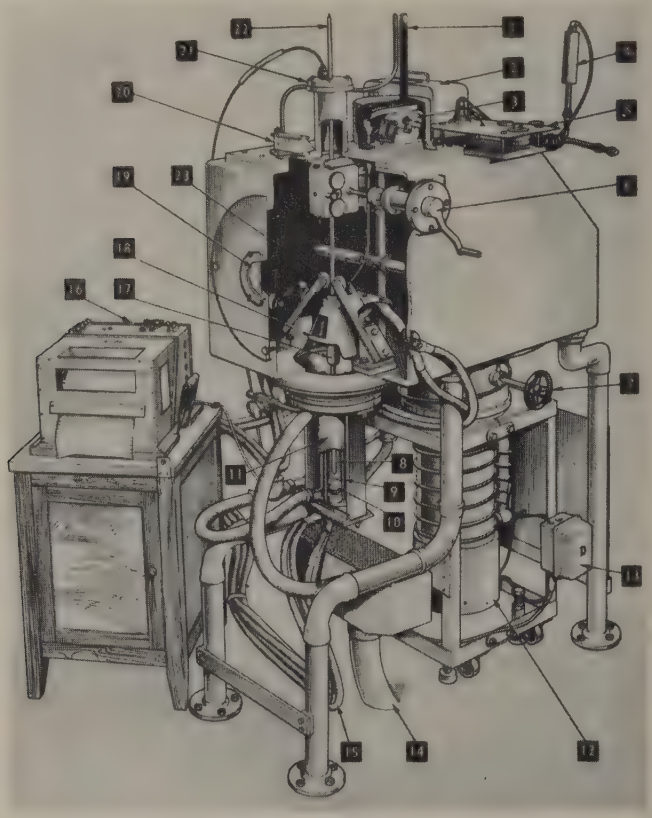

Fig. 3. A consumable-electrode arc-melting furnace*.

1. Alloy powder feed pipe
2. Vacuum gauge
3. Vibrator unit
4. Vacuum gauge head
5. Powder feed control panel
6. Electrode drive
7. Baffle valve
8. Consumable electrode
9. Water-cooled copper mould
10. Base plug
11. D.c. solenoid
12. Diffusion pump
13. Cut-off safety relays
14. To drain
15. High-current cables
16. Current and voltage recorder
17. Alloy powder distributor
18. Spatter guard
19. Observation window
20. Viewing periscope
21. Double Wilson-seal
22. Consumable electrode
23. Current conducting rolls

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a predetermined rate into the mould where they are melted by an arc drawn between the charge and a one-inch diameter water-cooled carbon electrode. The normal operating arc length (about two inches) is maintained by mechanically raising the electrode every time a compact falls from the hopper. The top plate carrying the non-consumable electrode may be removed and replaced with a device for feeding a consumable electrode. When double-melted ingots are required several of the first-melted ingots are joined together to form a 2 1/2-inch diameter consumable electrode which is then melted, in argon or high-vacuum, into a 5-inch diameter mould using either a.c. or d.c. The vacuum pumping unit comprises twin 9-inch diffusion pumps backed by a booster pump and rotary pump; the pumping speed is 2,000 litres per second, and during melting the chamber pressure is lower than 0.1 micron. During melting highly purified inert gas is continuously recirculated through the furnace and the calcium-type purifying unit. The use of such a system is extremely economical and it ensures a constant high-purity atmosphere at any desired pressure level; it prevents a build-up of contaminating gases as occurs in a static system.

A typical consumable-electrode furnace is shown in Fig. 3. The electrode is in the form of a rod 3/8 to 1 inch diameter and is pulled through a Wilson-seal by the drive mechanism into the mould via the current contact rollers. Alternatively, the electrode may be contained within a sealed "chimney" instead of having to pass it through a Wilson-seal. As illustrated, the alloy ingredients and deoxidants are contained in a tube and fed to the mould via a vibrating tray. Recently, however, a conveyor-belt type feeding mechanism has been used since it was found that the vibrating tray caused segregation of dissimilar-density alloys. For instance, when feeding molybdenum, titanium and carbon mixtures, the carbon and titanium were actually fed to the mould in batches as distinct from a steady stream of the mixture. Ingots up to 18 inches long and up to 4 inches diameter may be produced with a fixed water-cooled copper mould. Longer ingots are made in a semi-continuous casting device which is used in place of the conventional fixed mould. The vacuum pumping unit and inert-gas atmosphere arrangements are similar to those already described.

A special type of consumable-electrode furnace[1,7] is shown in Fig. 4. This was made to a design supplied by the Climax Molybdenum Co. and is suitable for producing molybdenum ingots up to 6 inches diameter. The electrode is continuously formed by feeding powder from a hopper into a spring-loaded collet-type die in which it is compressed every 1 or 2 seconds into a pellet by a hydraulically operated ram. The electrode leaving the bottom of the die is supported by water-cooled copper contacts, which also serve to introduce a sintering current which passes between these contacts and the die. The electrode, after this brief sintering, passes through the arc current contacts into the mould where, in making contact with the base plug, it initiates a metal-depositing arc. Thus the electrode is continuously melted and deposited into the mould to form an ingot.

In the arc-melting and pouring or "skull-melting" process a molten bath, produced with the aid of a consumable or non-consumable electrode, is bottom-poured or tilted into a mould to form a casting. As the charge is all molten at the time of pouring alloy segregation does not depend on the constancy of alloy feed to the melt, nor on the homogeneity of the electrode. Some freezing segregation of the conventional kind may occur in the mould when using certain alloys. In the past the process has mainly been used for the production of titanium and zirconium castings of up to about fifty

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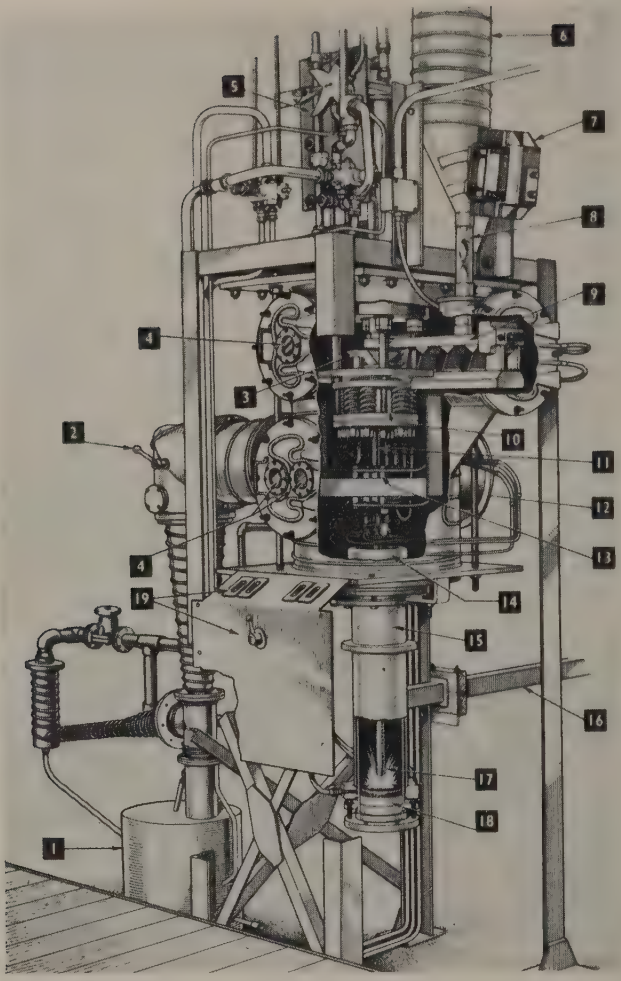

Fig. 4. Climax-type consumable-electrode arc-melting furnace*.

1. Booster pump
2. Baffle valve
3. Powder hopper (feeding pelleting die)
4. Inspection windows
5. Hydraulic ram mechanism
6. Raw material hopper
7. Hopper vibrator
8. Glass inspection tube
9. Vibrating tray
10. Spring loaded pellet forming die
11. Sintering zone
12. Bursting disc
13. Arc and sinter current contacts
14. Water-cooled copper mould (top)
15. Water-cooled copper mould
16. High-current bus-bar
17. Consumable electrode
18. Base plug
19. Controls

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pounds in weight; the process could be applied to most high-melting-point metals.

Fig. 5 shows a typical arc-casting furnace of the tilting type[8]. The equipment shown[9] in Fig. 6 was originally designed to minimise the problem of segregation which occurs in alloy melts when using the conventional type of "button furnace", this having only one crucible and no provision for pouring. It may be used for the prepa-

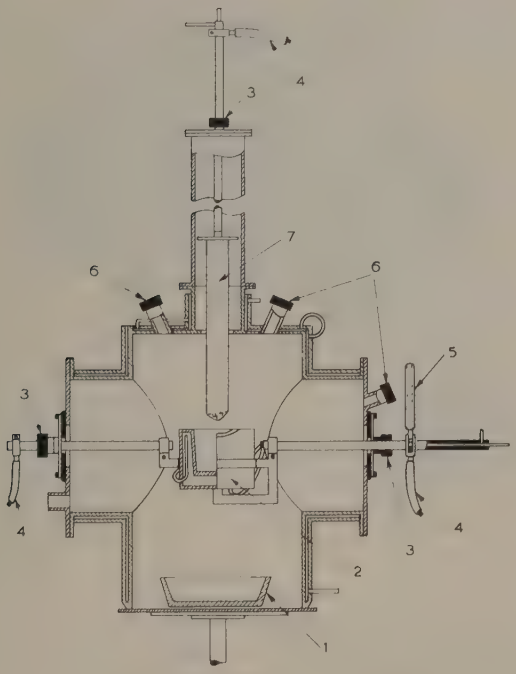

Fig. 5. A 15 lb. capacity tilting-type skull-melting furnace.

1. Graphite mould
2. Tilting crucible
3. "O" ring seal
4. Arc-current cable
5. Tilting mechanism
6. Inspection port
7. Electrode

ration of small castings of high-purity refractory alloys for research purposes, or for master alloys. The charge consists of either a solid piece of metal or of a pressed metal-powder compact and is placed in the larger of two interconnected water-cooled copper crucibles (Fig. 6) above which is a non-consumable electrode (the cathode). The arc runs between this electrode and the crucible (the anode) and is initiated by a high-frequency discharge in order to prevent damage to the crucible which would occur with contact arcing. When the charge is molten a hand-operated mechanism

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causes a portion of the melt to be tipped into the second crucible where it solidifies. Provision is made for the magnetic stabilisation of the arc, which is extinguished immediately after completion of pouring. An inert-gas atmosphere at a pressure of about 50 mm Hg is satisfactory and, in this, currents of up to 1200 A at an arc voltage of 20 to 30 V can be used.

Fig. 6. Arc-melting and pouring device.

ELECTRICAL SUPPLY EQUIPMENT

In consumable-electrode furnaces either a direct current or alternating current supply may be used. The choice of a particular current supply, for very large arc melting plants, appears to be determined mainly by the capital expenditure of the equipment. Although, on this basis, a.c. is usually the cheaper there are many large furnaces which use a d.c. supply. For experimental equipment, even of quite large size, d.c. is preferred since it is more adaptable and the polarity can be changed. Electrode polarity is determined by the atmosphere used and the metal being melted. For instance, with molybdenum, d.c. electrode negative polarity is used when melting in high vacuum, but in an argon atmosphere better results are obtained when the electrode is connected to the positive pole[10].

For non-consumable electrode furnaces a d.c. supply is essential, the electrode being connected to the negative pole; electrode losses are high if d.c. electrode-positive or an a.c. supply is used.

The prime requirement of a power source is that it must be capable of continuous operation at the desired current value and arc voltage, the latter varying between 20 and 50 V depending on the particular operating conditions. The minimum open

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ircuit supplied at the electrodes must be in excess of the arc-striking voltage; due llowance must be made for the potential drop along the leads from the power source. n general equipment similar to that used for conventional automatic arc-welding is ised and for this reason it is not described. For the d.c. supply motor-generators are videly used but increasing use has been made recently of transformer–rectifiers. Drift n the output arc-current must be avoided, especially when alloy ingredients are se- parately added in the consumable-electrode process. Drift may be minimised by run- ning the electrical supply, under load, for some time before melting commences[11]. Precautions must also be taken to avoid surges especially when melting in argon, otherwise there is a danger of auto-initiation of the arc[11].

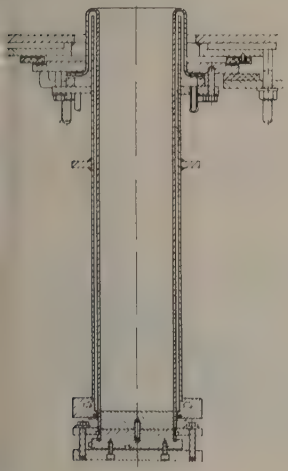

Fig. 7. Water-cooled copper mould suitable for production purposes.

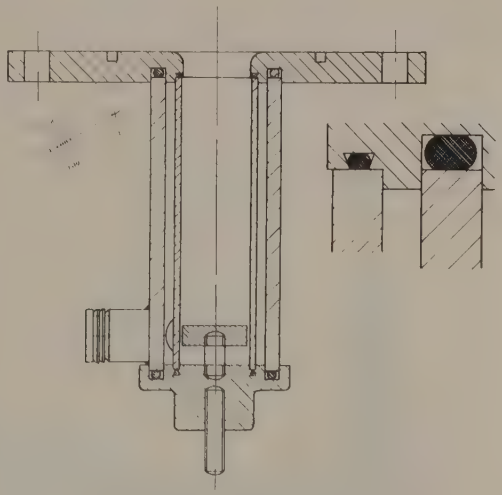

Fig. 8. Water-cooled copper mould suitable for experimental purposes*

MOULD DESIGN

Successful and safe operation of an arc-melting furnace demands the use of a well-lesigned and adequately cooled mould. Water-cooled copper moulds are usually used out an alternative safer coolant would be preferred. Precautions must be taken to minimise lime deposits and steam formation as these impair the heat-transfer charac- teristics and so increase the danger of mould penetration by the arc. The wall thick- ness of 2-inch diameter moulds should not be less than about $^3/_{16}$ inches. For larger liameter moulds greater thicknesses are required, not only to guard against arc pene- tration but also to provide a structure strong enough to resist the external pressure. The type of mould[3] shown in Fig. 7 is an efficient design and is suitable for moulds up to about 9 inches diameter. For small experimental moulds (up to 4 inches diameter)

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the type shown in Fig. 8 is convenient because, being made from standard bore copper pipe it is easily replaced. Although its design could be criticised owing to the position of the "O" ring seals it has been used satisfactorily for several years.

MAGNETIC STIRRING

To minimise alloy segregation in d.c. arc-melted ingots, also to minimise any tendency to arc-fixing, the molten pool may be stirred electro-magnetically by placing a d.c. solenoid around the mould. As the direction of arc-current flow through the molten pool is normal to that of the magnetic field a rotary motion must result and the direction of this can be determined by the application of Fleming's motor rule. The rate of stirring is controlled by both the arc current and the strength of magnetic flux. The optimum conditions are quite critical and must be determined experimentally.

The arc alone may be rotated around the molten pool by using a rotating horseshoe magnet outside the mould.

PLASMA-JET PROJECTOR AND CONSTRICTED-ARC TORCH

The conventional MAECKER[12] plasma-jet and WEISS[13] constricted-arc devices cannot be used satisfactorily for metallurgical purposes, such as melting, owing to the unavoidable presence of dissociated water vapour. In the device shown in Fig. 9 (100 kVA

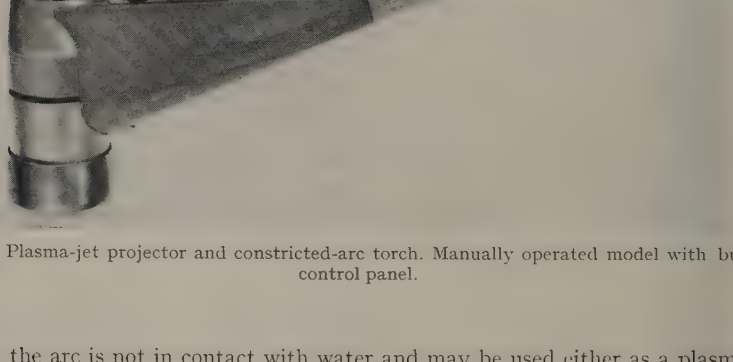

Fig. 9. Plasma-jet projector and constricted-arc torch. Manually operated model with built-in control panel.

model) the arc is not in contact with water and may be used either as a plasma-jet projector or as a constricted-arc torch simply by changing the electrical connections.

The device[14] shown in Figs. 9 and 10a consists, in principle, of a rod or tube-type electrode situated along the axis of, and insulated from, an intensively water-cooled nozzle-chamber which is at the opposite polarity. An electric arc formed between

References p. 72

hese two electrodes causes a plasma-jet to be projected from the nozzle. By passing stream of gas into the nozzle-chamber, or through the tubular central electrode he velocity of the jet and its temperature can be increased to a very high order.

When used as a constricted-arc torch (Figs. 9 and 10b) the electrical connections re basically to the central rod electrode and the workpiece only; the nozzle, serving nerely as a constricting device for the arc, should be electrically neutral. In practice, owever, the arc in such an arrangement may be unstable especially when the diameter f the nozzle orifice is small; to overcome this difficulty the circuit shown in Fig. 10b s employed. In this, provision is made for two simultaneous arcs, one between the entral electrode and the nozzle, and one between the central electrode and the workiece[15,16]. The current supplies for such twin arcing are obtained from two separate .c. power sources, or, alternatively, they may be obtained from a single source by the nsertion of a by-passing resistance as shown in Fig. 10b.

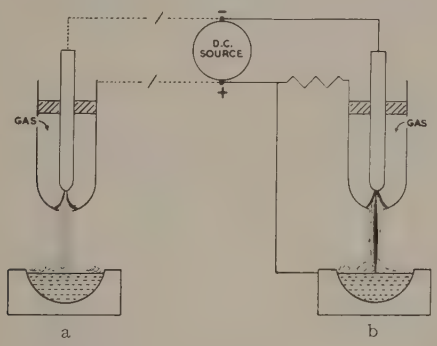

Fig. 10. Principle of the plasma-jet projector (left) and of the constricted-arc torch (right)

As the plasma-jet is an electric "flame", as distinct from a chemical one, its chemical composition is limited only by the reactivity of the electrodes; all the inert gases may be used. Owing to its exceedingly high temperature the plasma-jet can be used to melt all known substances whether metallic or non-metallic; some of the many present and potential applications include:

1. heating, melting, welding and "machining" of metallic or non-metallic materials;
2. determination of the resistance of materials to thermal shock or thermal fatigue;
3. purifying high-melting-point materials by preferential evaporation;
4. the growing of single crystals;
5. the production of chemical compounds, *e.g.* nitrides and silicides;
6. chemical synthesis and reduction;
7. spraying of metallic or non-metallic substances.

The prime function of the constricted-arc torch is for cutting, gouging, or "machining" ferrous or non-ferrous metals, although it may also be used for some of the applications listed above. The fundamental cutting mechanism is simply one of melting, the metal from the kerf being continuously melted by a high-intensity arc and

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blown away by a high-velocity high-temperature gas stream. In contrast the conventional gas cutting processes are based on an oxidation mechanism. There appears to be no metal nor alloy which cannot be cut by the constricted-arc process and the rate of cutting is generally very high. The optimum arc atmosphere has not yet been finalised for all metals but, at present, four main groups of media are being considered: argon with additions of hydrogen, nitrogen or hydrocarbons; nitrogen with additions of hydrogen or hydrocarbons; carbon dioxide mixtures; and gas–liquid or gas–powder-mixtures.

The plasma-jet projector and constricted-arc torch is not merely a scientific "tool" but a practical device which should be useful in many branches of technology.

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TECHNIQUES USED IN ALLOY INVESTIGATIONS AT TEMPERATURES ABOVE 1200°C

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INTRODUCTION

The present paper is confined to problems related to uranium and thorium and heir alloys. These materials are highly reactive and most of our difficulties are elated to this; some of the specific problems will be mentioned at appropriate points uring the description of the various techniques.

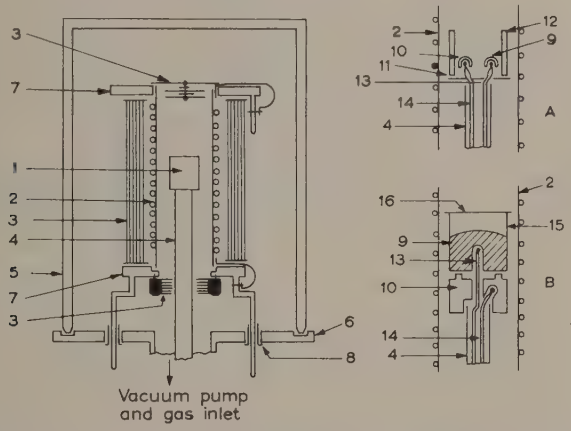

Fig. 1. Schematic arrangement of differential thermal analysis furnace chamber.

(1) specimen assembly (see A and B for details);
(2) furnace tube;
(3) molybdenum radiation shields;
(4) sillimanite support tube;
(5) water-cooled stainless steel bell jar;
(6) stainless steel base plate;
(7) water-cooled rings;
(8) polythene sleeve;
(9) sample;
(10) reference block;
(11) ceramic disc;
(12) nickel or molybdenum shield;
(13) sample thermocouple;
(14) comparison thermocouple;
(15) crucible;
(16) crucible lid.

THERMAL ANALYSIS

The layout of the thermal analysis furnace[1] is shown in Fig. 1. We are using the fferential technique which is immediately suited to automatic recording. Best sults are obtained with direct contact between the platinum–platinum/13% rho- um thermocouple and specimen (arrangement A) but reaction usually prevents this

eferences p. 76

from being used at high temperatures (the method has been used up to 1250°C). Using a crucible, the specimen (9) and reference material (10) are placed one above the other. Very few refractories can be used at high temperatures and although BeO has been used with some success for uranium, some contamination with beryllium occurs. The equipment can be used under a vacuum of better than 5×10^{-6} mm

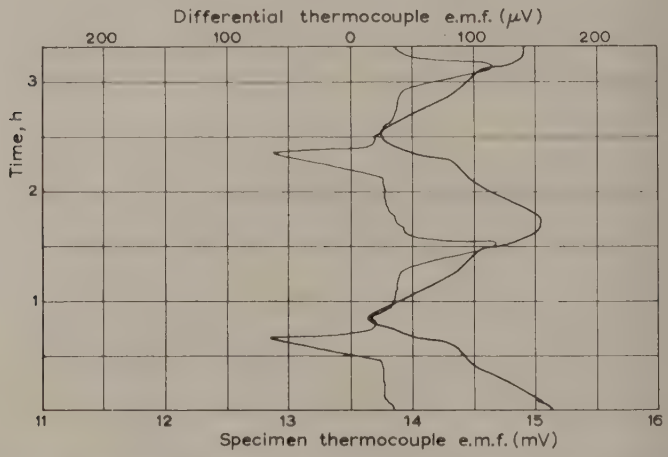

Fig. 2. Recorder trace given by thermal analysis equipment during automatic cycling through the melting point of a Th–35 at.-% Al alloy (1295°C). The lighter trace on the left is the differential e.m.f.; the darker trace on the right is the corresponding specimen temperature. Differential thermocouple pen writes 1/8 inch in front of specimen thermocouple pen on chart.

mercury or an inert atmosphere. The temperature is limited, not by the furnace which is molybdenum-wound and capable of temperatures in excess of 2000°C, but by electrical pick-up on the thermocouples which becomes significant above 1500°C. A typical result is shown in Fig. 2, which covers two cooling and two heating curves for a thorium–aluminium alloy, the specimen e.m.f. is recorded on the heavier trace and the differential e.m.f. on the lighter trace. Each peak on the differential curve is related to a kink in the heating or cooling curve.

ALLOY PREPARATION

Refractory troubles limit the use of high-frequency melting for thorium and many uranium alloys. The most satisfactory technique is arc-melting in which solid materials or powders may be melted. In the latter case loose powder is preferred since compacted powders tend to pick up large amounts of oxygen by surface oxidation of the original powder. It is normal to operate under a few centimeters of argon but with volatile materials, such as manganese, losses can be very much reduced by melting under a few atmospheres pressure of argon. The arc-furnace can be used for casting a variety of shapes but with very dense elements these techniques frequently lead to severe segregation. For example, it is difficult to cast homogeneous rods of uran-

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um carbon alloys since the carbide particles tend to float because of their low density. This effect is accentuated by the temperature gradient in the molten bar since the solubility of carbon in uranium decreases rapidly with decreasing temperature. Cast shapes have therefore to be used with care if misleading results are to be avoided.

The arc-furnace can also be used for determining melting points, as in the work of JONES, KNAPTON AND SAVILL[2], but we would like to indicate some of the difficulties. For example, for a series of thorium–aluminium alloys Fig. 3 compares the melting points obtained in the arc-furnace with the true melting points determined by thermal

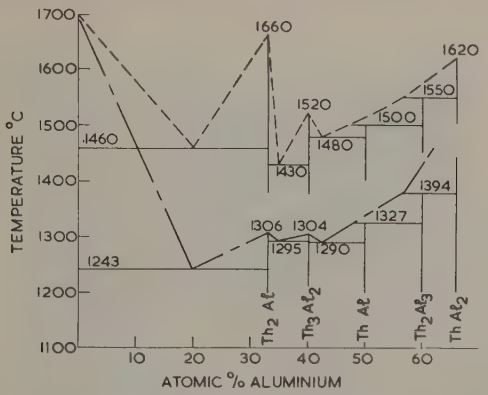

Fig. 3. Comparison of melting points in the thorium–aluminium system determined by thermal analysis (lower curve) and by the arc-furnace technique (upper curve).

nalysis. (The melting point of unalloyed thorium was not determined by thermal nalysis but the liquidus has been continued for clarity.) Note the common temperture axis. The arc-furnace melting points are indicated as being approximately 450°C and above whereas, apart from thorium, the true melting points are in the ange 1243–1394°C.

HEAT TREATMENT

The arc-furnace technique of homogenization is unsuitable for uranium and thorium lloys as no refractory metal is available which will stand prolonged contact above 350 C. Below this, molybdenum can often be used, but it is difficult to keep the pecimen temperature as low as 1300°C. Thus it is usually more convenient to seal he specimens in silica capsules in this temperature range since, by filling with argon hey will withstand temperatures of 1300°C. The alloys liquate with silica at about 50 C and hence molybdenum or tantalum foil has to be used to protect the specimens. Vith this technique filings for X-ray analysis can be satisfactorily annealed at temperatures up to 1300°C, providing care is taken to outgas both the silica and the foil efore sealing off. Alternatively, when necessary, specimens can be annealed in ontinuously pumped mullite tubes using conventional wire-wound furnaces.

For anneals at higher temperatures a bare molybdenum-wound high-vacuum arnace is used, the specimen still has to be supported but contamination is now

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restricted to the point of contact. Fig. 4 shows the 3/8 inch internal diameter, 3/4-inch long furnace with the molybdenum radiation shields opened out and the specimen lowered out of the furnace as in the initial outgassing. The furnace element is clamped onto water-cooled copper bars which are insulated from the base plate by the vacuum seals. Rapid quenching is obtained by a directed water or argon stream. Temperatures are measured with an optical pyrometer sighted vertically onto the specimen through a sliding window which enables viewing to be done under reproducible conditions. This furnace arrangement has the advantage of extreme simplicity but, if temperature measurements are to be reliable, specimens must be small and have a "sighting" hole drilled in their upper surface (see Fig. 4).

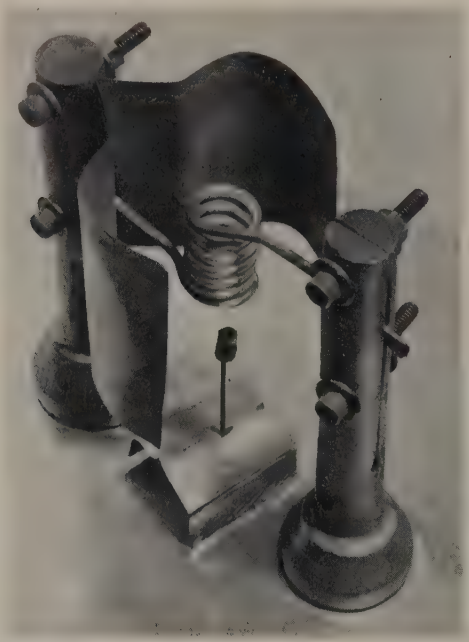

Fig. 4. High temperature furnace. The spiral of molybdenum wire is clamped in 1/2-inch diameter water-cooled copper electrodes. The specimen has been lowered as for the initial outgassing and the radiation shields opened for the photograph.

CONCLUSIONS

Existing techniques for attaining temperatures above 1200°C are usually adequate for our work, the troubles encountered being mainly due to the extreme reactivity of our samples with all metal and ceramic containers and any residual gas in the vacuum system. With experience it has usually been possible to obtain considerable information on alloys at temperatures up to 2000°C.

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A MOLYBDENUM RESISTANCE COOLING CURVE FURNACE

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INTRODUCTION

A considerable difficulty is presented in fundamental research on solidification by the interpretation of cooling curves. An attempt has been made to overcome this difficulty by constructing a cooling curve furnace which gives an approximately uniform rate of loss or gain of heat over small temperature ranges.

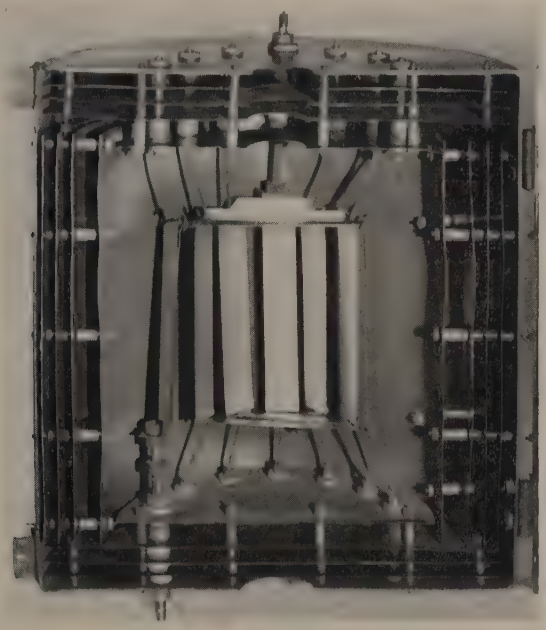


Fig. 1.

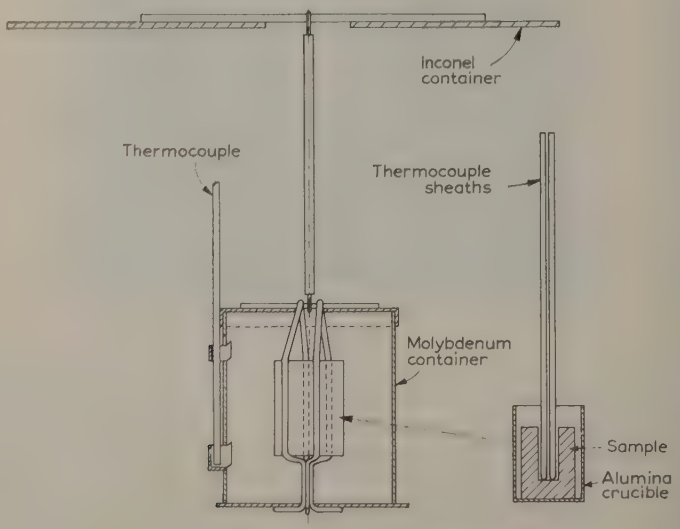
There are two methods commonly used to obtain cooling curves. In the simplest and more usual technique the power to the furnace is reduced and the furnace and sample cool simultaneously. The rate at which heat is lost from the sample is governed by the temperature difference between the furnace and the ingot. At an arrest, the furnace continues to cool so that the temperature difference between the sample and the furnace becomes greater as the arrest continues. This results in an increasing rate of heat loss from the sample.

In the alternative technique the sample is removed from the hot portion of the furnace either to a cooler furnace or to a cool zone of the original furnace. This corresponds to the condition in which the ingot is enclosed in a constant temperature environment; and would give a constant rate of loss of heat during a transformation if it took place at a constant temperature. Unfortunately, in many cases undercooling and recalescence occurs and the rate of heat loss changes.

It was because of these difficulties that the new technique described in this note was developed. An attempt has been made to maintain a constant temperature difference between the sample and its environment, so that for many purposes the rate of heat loss from the sample can be considered as uniform during an arrest. If, for example, we consider a transformation occurring over a 50°C range of temperature, with a constant temperature difference between the sample and its environment of 200°C, it will be seen that there is a change in rate of heat loss of only 11% between the extremes of temperatures. Furthermore, the rate of heat loss can easily be calculated exactly. This method has the additional advantage that the cooling rate can be rapidly adjusted to a pre-determined value during the cooling of the sample.

It was decided that the furnace must have an upper temperature limit of at least 1600°C. In addition, a wide range of possible cooling rates was required, and a choice of melting either in vacuum or in hydrogen or nitrogen atmospheres.

In order to control the temperature difference between the sample and the furnace environment there are two further requirements. First, the environment temperature must be uniform, and secondly there must be little temperature lag between the environment temperature and the control. In practice, this means that the furnace must have a very low heat content. These requirements are fulfilled in the furnace shown in Fig. 1.



Section of sample assembly

Fig. 2.

DESIGN OF THE FURNACE

There are several unusual details in the design. A suspended molybdenum tape heating element completely surrounds the specimen (Fig. 1), and the entire furnace is built inside a hinged container made of "Inconel". The heating element is supported directly from this container by means of 1.5 mm molybdenum wires which are insulated over the portion that passes through the four molybdenum radiation shields. The two halves of the heater are connected in series and so arranged that the two together act as a non-inductive winding. This eliminates the low frequency pick-up which is troublesome with some types of electronic recorders.

The sample is placed in an alumina crucible at the centre of a molybdenum can, which effectively smooths temperature gradients around the sample and responds very rapidly to changes in temperature of the heated tape. Three thermocouples are set up, one located in a pocket in the molybdenum can, and two at the centre of the sample (Fig. 2). The furnace is then closed round the crucible assembly and the whole is placed in a water-cooled evacuated chamber.

The control system operates on the difference in e.m.f. between the thermocouple in the molybdenum can and one of the thermocouples in the sample. If the e.m.f. changes from a pre-set value, the furnace power is automatically altered to counteract the change.

Besides the control of heat loss, the technique has other advantages. An obvious one is the increase in the definition with which arrests are shown. This is illustrated by Fig. 3. A cooling curve for a 27 g sample that exhibited little undercooling is shown as a solid line. The broken line is a theoretical curve indicating the result that would be expected with the usual cooling furnace technique.

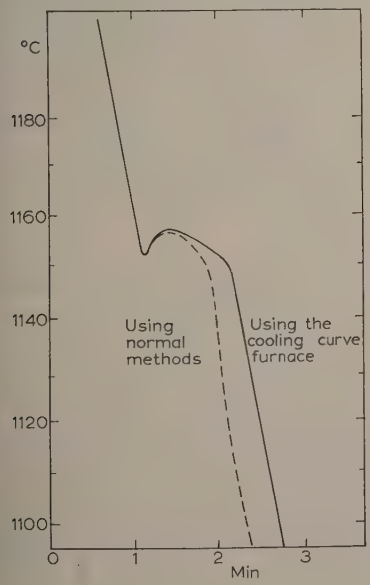


Fig. 3.

It is necessary to replace the complete thermocouple assembly after each experiment, in order to avoid errors due to contamination of the thermocouples. Difficulties have also arisen due to the formation of a molybdenum coating on the ceramic insulators, rendering them conductive. This should be largely prevented by putting small radiation shields to each of the heating element supports.

At present the furnace is still under development. It has so far been operated only at temperatures up to 1400°C, while trials have been carried out using various control systems. When the control system has been perfected this furnace should be ideal for detailed investigations concerning crystallization rates and similar phenomena at high temperatures.

ARC FURNACE AND ELECTRON BOMBARDMENT TECHNIQUES USED IN STUDIES OF THE REFRACTORY METALS

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INTRODUCTION

During recent years the arc furnace has given a complete change of outlook on the problem of alloy preparation or consolidation of refractory and highly reactive metals. At the A.E.I. Research Laboratory, arc furnaces have been in constant use for nine years and this paper includes certain of the techniques developed. Also, possible applications of electron bombardment heating as a complementary technique are briefly discussed.

THE ARC FURNACE

A cross section of one of our argon-arc furnaces is given in Fig. 1. The furnace was designed for flexibility of operation and allows of quick interchange of hearth shapes. This is accomplished by mounting each hearth on a standard size of brass flange which is held between two rubber seals in the assembled furnace. The hearths are simple, inexpensive and easy to prepare shaped to produced ingots of special forms.

A 1/4-inch diameter tungsten electrode, brazed into a water cooled copper block, is normally used with this furnace, and with the exception of certain materials attacking the electrode, no tungsten contamination has been detected in alloy melts using this arrangement.

A further feature of this furnace is that it is readily adapted for use as a semi continuous casting furnace (Fig. 2). Ingots up to 12 inches in length and 1 inch diameter can be built up from material fed in through one of the side ports of the furnace.

MELTING POINT DETERMINATIONS

Several papers on alloy phase diagram investigations have been published from this Laboratory incorporating liquidus values obtained by an optical pyrometer technique in the argon-arc furnace.

The technique is shown in Fig. 3. It consists of maintaining a small bead (0.5–1.0 cm diameter) partly in the molten state and sighting a disappearing filament optical pyrometer *just on the liquid side* of the liquid–solid junction. The mean of ten to twelve readings is taken to give an "observed melting point" value. The liquidus value is then obtained from the observed melting points of a number of pure metals ranging from nickel melting at 1455°C to tungsten (3400°C). As shown in Fig. 4, the plot is nearly linear. The values obtained are assumed to approximate to the liquidus rather than the solidus curve in view of the fact that observations are made on the all liquid portion of the bead.

If the effect of emissivity variation only on the apparent temperature of a hot body is considered, it is hardly surprising that the observed melting points of the pure metals do not depart markedly from a single curve. Fig. 5 shows curves corresponding to emissivity values of 0.3, 0.4 and 0.5. At 3000°C, a variation of 0.3–0.5 gives only a ± 50°C change in observed melting point. The standard metals are included in Fig. 5 and are grouped around an emissivity value of 0.45.

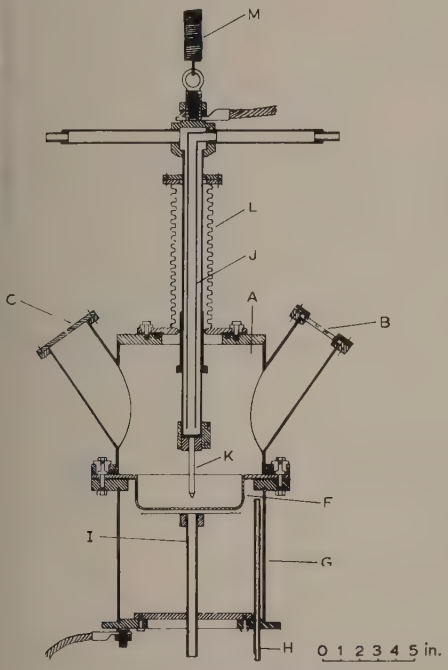

Fig. 1. Laboratory arc furnace.

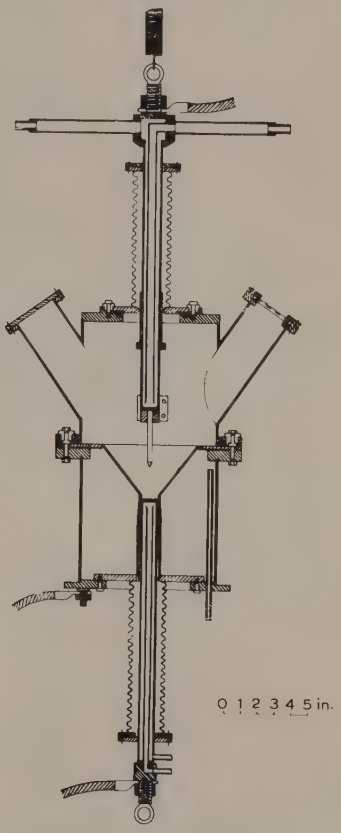

Fig. 2. Continuous casting arc furnace.

Not all metals conform with this emissivity value in the liquid state. One example is rhenium. The melting point of this metal is well established by classical methods at 3170°C, but the optical method gives a value which is consistently 180°C low if an emissivity value of 0.45 is assumed. Thus it appears that rhenium has a low emissivity (near 0.3) in the liquid state.

Another high melting point metal, osmium, has been examined by this technique. The melting point does not appear to have been determined accurately by other

methods, but is reported in the literature as 2750 ±100°C. The optical pyrometer method gives an observed value of 2660°C for osmium, and it is suggested that the melting point of osmium is higher than the reported value and lies in the range 3000–3100°C.

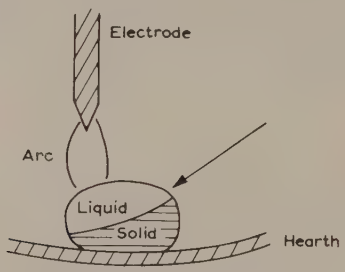

Fig. 3. Melting point determination in arc furnace.

In an alloy system, if the melting points of the components are accurately known, it is more satisfactory to assume a linear variation of true:observed correction factor across the system rather than using the correction curve previously described

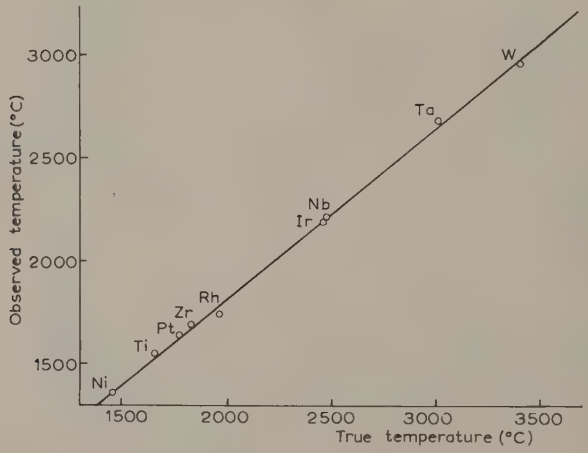

Fig. 4. Correction curve.

ANNEALING IN THE ARC FURNACE

It is possible to anneal alloy specimens, albeit rather unevenly, by direct heating in the arc on the water cooled copper hearth of the arc furnace. This is frequently of use, *e.g.* for homogenisation anneals, immediately subsequent to alloying.

Another method of annealing employs metal blocks as containers for small speci-

mens in the arc furnace. Molybdenum blocks have been widely used for annealing molybdenum-base alloys in the range 1800–2400°C. The blocks rest on the hearth of the arc furnace, and in order to minimise temperature gradients the area of contact with the hearth is restricted to three small points by appropriately shaping the base of the block. Horizontal holes, 5 mm diameter, plugged at each end with molybdenum plugs are used to contain the samples being annealed. Temperature measurements

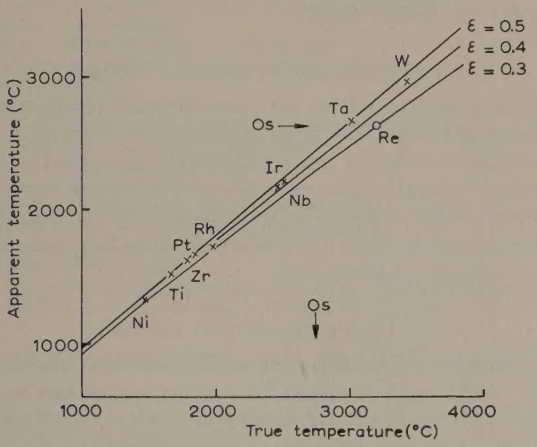

Fig. 5. Effect of emissivity (ε) on apparent temperature.

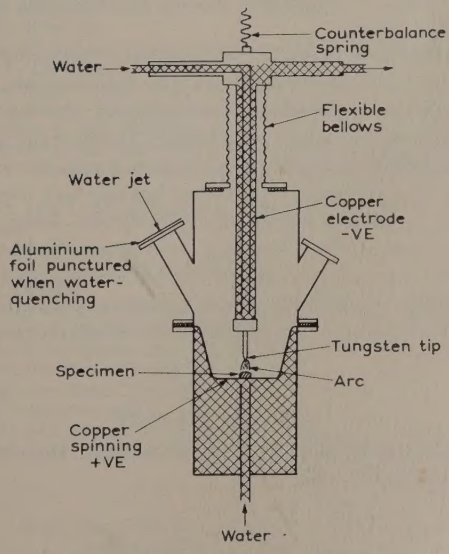

Fig. 6. Water quenching arc furnace.

are taken by optical pyrometer methods through 2 mm sighting holes bored into the specimen chamber.

This method of annealing has much to commend it. It is readily applicable by anyone possessing an arc furnace; the atmosphere of gettered argon is not a source of contamination, and metallic contamination can be made least objectionable by selecting the appropriate material for the blocks. In this Laboratory, molybdenum blocks have been used for molybdenum alloys, or tungsten, niobium and zirconium blocks for alloys of these as base metals.

WATER QUENCHING IN THE ARC FURNACE

If it is required to cool rapidly from the heat treatment temperature, this may be done by water quenching in the arc furnace (Fig. 6). A container of water approximately equal in volume to the arc furnace chamber is attached to the side arm of the furnace. The water is retained by an aluminium foil diaphragm which is punctured to flood the hearth of the furnace at the completion of the anneal. Molybdenum annealing blocks of several hundred grams in weight have been successfully quenched from temperatures near the melting point.

ELECTRON BOMBARDMENT HEATING

It is possible to regard an electron gun as a similar, but alternative method of heating to an arc; techniques developed for arc furnaces should be fairly generally applicable with electron bombardment heating on a water cooled copper hearth.

By its nature, the electron bombardment process requires a good vacuum for its successful operation. This may be difficult to achieve if the material gases badly or has a high vapour pressure. However, if gas evolution is slow, advantage may be taken of the high vacuum to degas metals such as vanadium, niobium or tantalum to a very low hardness value.

Another basic difference between arc and electron bombardment heating is in the magnitudes of the electric currents involved. The high currents required for heating in a stable arc result in considerable electromagnetic stirring effects in the melt. Stirring is advantageous for alloy preparation, but certain applications such as flotation of impurities from uranium metal, require a non-stirred melt.

The arc is also a very concentrated form of heating and there is little control of the size or position of the area heated. By appropriate design of electron gun and with simple lenses it is possible to heat any desired area by electron bombardment, from very small spots, as may be required for fine welding applications, upwards.

A further factor in favour of electron bombardment heating is that power supplies for laboratory applications are cheaper than low voltage d.c. generators required by arc furnaces.

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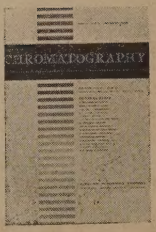

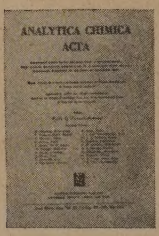

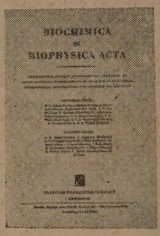

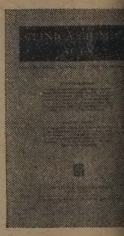

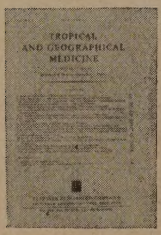

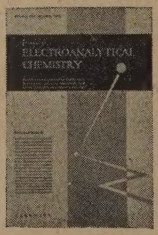

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